Efficient and Stereoselective Dimerization of Pyrroloindolizine Derivatives Inspired by a Hypothesis for the Biosynthesis of Complex Myrmicarin Alkaloids.

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Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottomed flasks or in oven-dried 5 mm o.d. NMR tubes. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Where necessary (so noted), solutions were deoxygenated by bubbling through with balloon-pressure argon through for the time stated. Where noted, compounds were dried azeotropically by concentrating three times from benzene under high-vacuum (0.1 Torr), refilling the flask with argon between each cycle. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and an aqueous solution of ceric ammonium molybdate (CAM). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C.

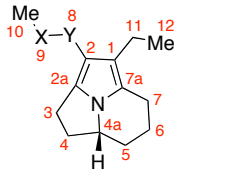
Materials. Commercial reagents and solvents were used as received with the following exceptions:

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

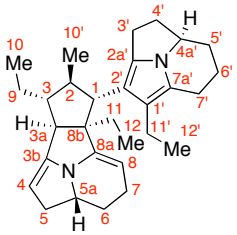
dichloromethane, diethyl ether, tetrahydrofuran, and triethylamine were purified by the method of Grubbs et al. under positive argon pressure.[2] Dimethylsulfoxide (>99.9 % HPLC grade, ≤0.020 % water) was used as received. Benzene and 2,6-lutidine were distilled over calcium hydride, and dimethylformamide was distilled over calcium sulfate under reduced pressure. Triethylsilyl trifluoromethanesulfonate and triisopropyl trifluoromethanesulfonate were distilled under reduced pressure. Deuterated solvents were used as received.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with an inverse probe 500 MHz, a 500 MHz, or an inverse probe 600 MHz spectrometer, are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent (C_6D_5H: δ 7.16, $CHCl_3$: δ 7.27). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a 500 MHz spectrometer, are recorded in parts per million from internal tetramethylsilane on the δ scale, and are referenced from the carbon resonances of the solvent (C_6D_6: δ 128.39, $CDCl_3$: δ 77.23). Infrared data (IR) are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High resolution mass spectra were obtained using a Fourier transform ion cyclotron resonance mass spectrometer with electrospray ionization.

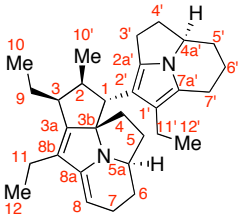
Compound Numbering. The numbering system for proton and carbon assignments for all pyrroloindolizine structures is consistent with the isolation reports for the naturally occurring tricyclic myrmicarins.[3] The numbering system for proton and carbon assignments for all heterodimeric structures is consistent with the isolation reports for myrmicarin 430A[4] and the numbering system of isomyrmicarin 430A.[5]



Myrmicarin
(–)-(R) 215A: X-Y = (*Z*)-CH=CH
(+)-(R) 215B: X-Y = (*E*)-CH=CH
(+)-(R) 217: X-Y = CH_2–CH_2

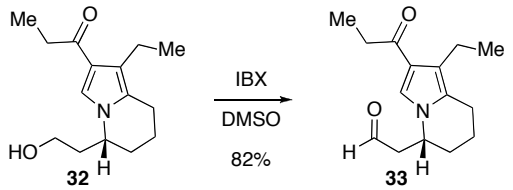


Myrmicarin 430A



Isomyrmicarin 430A

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
[3] Schröder, F.; Franke, S.; Francke, W. *Tetrahedron* **1996**, 52, 13539–13546.
[4] Schröder, F.; Sinnwell, V.; Baumann, H.; Kaib, M. *Chem. Commun.* **1996**, 2139–2140.
[5] Ondrus, A. E.; Movassaghi, M. *Tetrahedron* **2006**, *62*, 5287–5297.

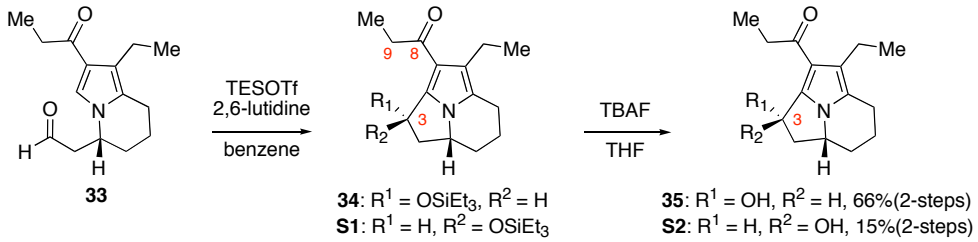


(1-Ethyl-2-propionyl-5,6,7,8-tetrahydro-indolizin-5-yl)-acetaldehyde (33):

A solution of 2-iodoxybenzoic acid[6] (IBX, 620 mg, 2.21 mmol, 1.10 equiv) in anhydrous dimethylsulfoxide (DMSO, 2.50 mL) was prepared by sonicating the initial suspension for 30 min, and this solution was then degassed (argon purge, 10 min). The solution of IBX was added dropwise via cannula to an anhydrous and degassed (argon purge, 10 min) solution of alcohol **32**[7] (502 mg, 2.01 mmol, 1 equiv) in dimethylsulfoxide (10.0 mL), causing the solution to turn deep rose within 2 min. After 1 h, an additional portion of 2-iodoxybenzoic acid (620 mg, 2.21 mmol, 1.10 equiv) in dimethylsulfoxide (2.50 mL) was prepared and degassed as above and added to the reaction mixture via cannula. After an additional 2 h, the deep rose solution was partitioned between diethyl ether (10 mL) and a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (10:1, 10 mL). The resulting mixture was diluted with additional portions of diethyl ether (70 mL) and saturated aqueous sodium thiosulfate solution-saturated aqueous sodium bicarbonate solution (10:1, 60 mL), then the aqueous phase was separated from the clear, pale yellow organic phase and extracted with diethyl ether (5 × 60 mL). The combined organic phases were washed with brine (50 mL), were dried over anhydrous sodium sulfate, and were concentrated in vacuo. The resulting brown residue was purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine and 32.5 → 57.5% ethyl acetate in hexanes, diameter: 4.0 cm, height: 6.0 cm) to afford the aldehyde **33** as a pale yellow oil (408 mg, 82%).

^{1}H NMR (500 MHz, C_6D_6, 20°C):	9.02 (t, *J* =1.1 Hz, 1H, C**H**O), 6.77 (s, 1H, NC**H**=C), 3.99 (ddd, *J* = 11.3, 6.7, 5.1 Hz, 1H, NC**H**CH_2), 2.93–3.04 (m, 2H, CC**H**$_2CH_3$), 2.23 (m, 2H, NCC**H**$_2CH_2$), 2.03 (ddd, *J* = 18.2, 5.1, 1.1 Hz, 1H, NCHC**H**$_2$CHO), 1.83 (ddd, *J* = 18.2, 6.7, 1.1 Hz, 1H, NCHC**H**$_2$CHO), 1.41 (t, *J* = 7.5 Hz, 3H, CCH_2C**H**$_3$), 1.36–1.40 (m, 1H, NCHC**H**$_2CH_2$), 1.26 (t, *J* = 7.4 Hz, 3H, $COCH_2$C**H**$_3$), 1.00–1.24 (m, 3H, NCHC**H**$_2CH_2$, $NCHCH_2$C**H**$_2$).
^{13}C NMR (125.8 MHz, C_6D_6, 20°C):	198.5, 196.1, 128, 127.3, 123.5, 122.7, 50.4, 49.3, 33.3, 29.4, 21.5, 19.0, 18.5, 16.1, 9.7.
FTIR (neat) cm^{-1}:	2936 (s, C–H), 2730 (m, C–H), 1723 (s, C=O), 1688 (s, C=O), 1650 (s), 1516 (m), 1380 (m).
HRMS–EI (*m/z*):	calcd for $C_{15}H_{22}NO_2$ $[M + H]^+$: 248.1645, found: 248.1654.
TLC (silica gel, 50% EtOAc–hexanes), *Rf*:	0.39 (UV, CAM).

[6] Prepared according to the procedure of Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537-4538.
[7] Movassaghi, M.; Ondrus, A. E. *Org. Lett.* **2005**, *7*, 4423–4426.



1-(1-Ethyl-3-hydroxy-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl)-propan-1-one (35):

Triethylsilyl trifluoromethanesulfonate (TESOTf, 1.08 mL, 4.79 mmol, 3.30 equiv) was added dropwise via syringe to a colorless and anhydrous solution of aldehyde **33** (358 mg, 1.45 mmol, 1 equiv) and 2,6-lutidine (845 μL, 7.25 mmol, 5.00 equiv) in benzene (30.0 mL), producing an intense yellow solution. After 15 min, the reaction flask was placed on an ice-water bath for 3 min, then saturated aqueous sodium bicarbonate solution (35 mL) was added and the reaction flask was immediately removed from the ice-water bath. This mixture was diluted with diethyl ether (60 mL) and the aqueous phase was separated from the yellow organic phase and extracted with diethyl ether (3 × 20 mL). Aqueous hydrochloric acid solution (1N, 100 mL) was added to the combined organic phases and the biphasic mixture was agitated thoroughly (~3 min) in a separatory funnel until TLC analysis indicated that the C8-C9 silyl enol ethers had been completely hydrolyzed to the C8 ketone. The aqueous phase was separated from the yellow organic phase and extracted with diethyl ether (2 × 30 mL), then the combined organic phases were washed sequentially with saturated aqueous sodium bicarbonate solution (35 mL) and brine (35 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give crude **34** and **S1**.

Tetrabutylammonium fluoride (TBAF, 1.0 M in tetrahydrofuran, 5.08 mL, 5.08 mmol, 3.50 equiv) was added via syringe to a solution of the crude yellow residue in tetrahydrofuran (THF, 7.25 mL) at 0 °C in an ice-water bath. After 15 min, ethyl acetate (5 mL) and water (5 mL) were added simultaneously and the reaction flask was immediately removed from the ice-water bath. The mixture was diluted with additional portions of ethyl acetate (30 mL), water (10 mL), and brine (1.5 mL). The aqueous phase was separated from the yellow organic phase and extracted with ethyl acetate (5 × 15 mL). The combined organic phases were washed with brine (15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to give a yellow residue. This residue was purified by flash column chromatography on silica gel (eluent: 45 → 75% ethyl acetate in hexanes, diameter: 4.0 cm, height: 23 cm) to afford the tricyclic alcohols **35** (237 mg, 66%) and **S2** (52.3 mg, 15%) as white powders.

Ketone 34:

^{1}H NMR (500 MHz, C_6D_6, 20°C): 5.17 (dd, *J* = 7.6, 6.1 Hz, 1H, C3–H), 3.32 (dq, *J* = 16.8, 7.4 Hz, 1H, C9–H), 3.08–3.18 (m, 2H, C11–H, C11–H'), 2.92 (tdd, *J* = 10.8, 5.4, 3.2 Hz, 1H, C4a–H), 2.86 (dq, *J* = 16.8, 7.3 Hz, 1H, C9–H'), 2.43 (ddd, *J* = 16.4, 6.5, 1.1 Hz, 1H, C7–H_c), 2.31 (dt, *J* = 11.7, 5.7 Hz, 1H, C4–H_c), 2.17 (ddd, *J* = 16.3, 12.0, 6.9 Hz, 1H, C7–H_t), 1.70 (ddd, *J* = 11.3, 10.5, 7.8 Hz, 1H, C4–H_t), 1.53–1.58 (m, 1H, C6–H_t), 1.51 (t, *J* = 7.5 Hz, 3H, C12–H), 1.44 (t, *J* = 7.3 Hz, 3H, C10–H), 1.39 (dq, *J* = 12.5, 3.4 Hz, 1H, C5–H_c), 1.17 (tddd, *J* = 13.4, 12.3, 6.5, 2.8 Hz, 1H, C6–H_c), 0.96 (t, *J* = 7.9 Hz, 9H, $SiCH_2C\mathbf{H}_3$), 0.77 (tdd, *J* =

12.9, 11.2, 2.6 Hz, 1H, C5–H_t), 0.59 (q, *J* = 7.9 Hz, 6H, SiC**H**$_2$CH$_3$).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 196.4, 137.1, 127.3, 120.2, 118.0, 72.4, 53.4, 47.5, 35.7, 29.5, 22.2, 20.2, 19.9, 16.3, 9.3, 7.5, 5.7.

FTIR (neat) cm^{-1}: 2956 (s, C–H), 1650 (s, C=O), 1491 (m), 1321 (m), 1118 (s).

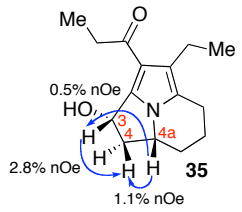
HRMS–EI (*m*/*z*): calcd for $C_{21}H_{35}NO_2SiNa$ [M + Na]$^+$: 384.2329, found: 384.2335.

TLC (silica gel, 10% EtOAc–hexanes), *Rf*: 0.28 (UV, CAM).

Tricyclic alcohol 35:

^{1}H NMR (500 MHz, C_6D_6, 23°C): 6.11 (s, 1H, C3–OH), 5.35 (dd, *J* = 8.2, 6.4 Hz, 1H, C3–H), 2.92 (dddd, *J* = 11.2, 10.3, 5.2, 3.9 Hz, 1H, C4a–H), 2.74 (dq, *J* = 17.2, 7.0 Hz, 1H, C11–H), 2.67 (dq, *J* = 17.2, 7.0 Hz, 1H, C11–H'), 2.53 (dq, *J* = 10.7, 7.4 Hz, 1H, C9–H), 2.52 (dq, *J* = 10.7, 7.4 Hz, 1H, C9–H'), 2.47 (ddd, *J* = 11.7, 6.3, 5.4 Hz, 1H, C4–H_c), 2.31 (ddd, *J* = 16.5, 6.7, 1.2 Hz, 1H, C7–H_c), 2.10 (ddd, *J* = 16.5, 11.9, 7.0 Hz, 1H, C7–H_t), 1.90 (ddd, *J* = 11.8, 10.2, 8.2 Hz, 1H, C4–H_t), 1.47 (ddddd, *J* = 13.9, 6.9, 4.1, 2.7, 1.4 Hz, 1H, C6–H_t), 1.24 (t, *J* = 7.2 Hz, 3H, C12–H), 1.21–1.27 (m, 1H, C5–H_c), 1.13 (t, *J* = 7.5 Hz, 3H, C10–H), 1.07 (tddd, *J* = 13.5, 11.8, 6.6, 2.7 Hz, 1H, C6–H_c), 0.66 (tdd, *J* = 12.9, 11.3, 2.6 Hz, 1H, C5–H_t).

nOe data (500 MHz, C_6D_6, 20°C):

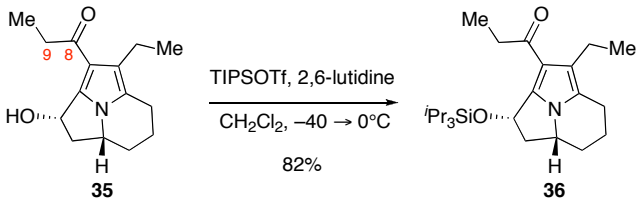


^{13}C NMR (125.8 MHz, $CDCl_3$, 20°C): 201.0, 142.9, 123.8, 121.6, 118.0, 70.3, 56.0, 46.3, 34.3, 30.1, 22.4, 20.5, 20.1, 16.7, 9.1.

FTIR (neat) cm^{-1}: 3346 (m, O–H), 2942 (m, C–H), 1609 (s, C=O), 1498 (s), 1452 (m), 1253 (m).

HRMS–EI (*m*/*z*): calcd for $C_{15}H_{21}NO_2Na$ [M + Na]$^+$: 270.1464, found: 270.1461.

TLC (silica gel, 60% EtOAc–hexanes), *Rf*: 0.57 (UV, CAM).

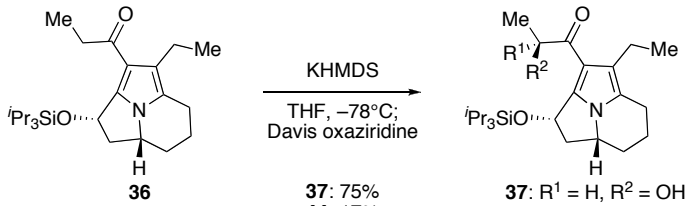


35 36

1-[1-Ethyl-3-(triisopropyl-silanyloxy)-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl]-propan-1-one (36): Triisopropyl trifluoromethanesulfonate (TIPSOTf, 500 μL, 1.86 mmol, 2.26 equiv) was added dropwise via syringe to a clear yellow solution of tricyclic alcohol **35** (204 mg, 825 μmol, 1 equiv) and 2,6-lutidine (480 μL, 4.12 mmol, 5.00 equiv) in dichloromethane (12.0 mL) at –40 °C. The resulting intense yellow solution was maintained at –40 °C for 2 min, and then the reaction flask was placed on an ice-water bath. After 15 min, saturated aqueous sodium bicarbonate solution (15 mL) was added and the reaction flask was removed from the ice water bath. The mixture was diluted with diethyl ether (50 mL) and the layers were separated. The yellow organic phase was extracted with diethyl ether (3 × 15 mL). Aqueous hydrochloric acid solution (1N, 60 mL) was added to the combined organic phases and the biphasic mixture was agitated thoroughly (~8 min) in a separatory funnel until TLC analysis indicated that the C8-C9 silyl enol ether had been completely converted to the C8 ketone **36**. The aqueous phase was extracted with diethyl ether (2 × 30 mL), and the combined organic phases were washed sequentially with saturated aqueous sodium bicarbonate solution (25 mL) and brine (25 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to a yellow residue. This residue was purified by flash column chromatography on silica gel (eluent: 3.5% triethylamine, 1% ethyl acetate, and 6% dichloromethane in hexanes, diameter: 4.0 cm, height: 19 cm) to afford the triisopropylsilyl ether **36** (273 mg, 82%) as a white powder.

^{1}H NMR (500 MHz, C_6D_6, 20°C):	5.38 (dd, *J* = 7.8, 6.1 Hz, 1H, C3–H), 3.38 (dq, *J* = 17.1, 7.3 Hz, 1H, C9–H), 3.16 (dq, *J* = 13.7, 7.0 Hz, 1H, C11–H), 3.04 (dq, *J* = 13.7, 7.1 Hz, 1H, C11–H'), 2.91 (dq, *J* = 17.1, 7.3 Hz, 1H, C9–H'), 2.89 (tdd, *J* = 10.7, 5.4, 3.3 Hz, 1H, C4a–H), 2.43 (ddd, *J* = 16.1, 6.6, 1.1 Hz, 1H, C7–H_c), 2.41 (dt, *J* = 11.4, 5.7 Hz, 1H, C4–H_c), 2.17 (ddd, *J* = 16.3, 12.2, 6.9 Hz, 1H, C7–H_t), 1.79 (ddd, *J* = 11.3, 10.5, 7.8 Hz, 1H, C4–H_t), 1.56 (ddddd, *J* = 13.7, 6.8, 4.1, 2.7, 1.4 Hz, 1H, C6–H_t), 1.49 (t, *J* = 7.4 Hz, 3H, C12–H), 1.44 (t, *J* = 7.3 Hz, 3H, C10–H), 1.40–1.45 (m, 1H, C5–H_c), 1.19 (tddd, *J* = 13.4, 12.2, 6.5, 2.9 Hz, 1H, C6–H_c), 1.01–1.12 (m, 21H, SiC**H**$(CH_3)_3$, SiCH$(CH_3)_3$), 0.84 (tdd, *J* = 12.8, 11.2, 2.6 Hz, 1H, C5–H_t).
^{13}C NMR (125.8 MHz, C_6D_6, 20°C):	196.5, 137.0, 127.0, 120.0, 118.2, 73.3, 53.2, 47.4, 35.8, 29.6, 22.2, 20.1, 20.0, 18.7, 18.6, 16.4, 13.6, 9.1.
FTIR (neat) cm^{-1}:	2867 (s, C–H), 1650 (s, C=O), 1489 (s), 1256 (m), 1123 (m).
HRMS–EI (*m/z*):	calcd for $C_{24}H_{41}NO_2SiNa$ $[M + Na]^+$: 426.2799, found: 426.2791.

TLC (silica gel, 12.5% EtOAc–hexanes), *Rf*: 0.33 (UV, CAM).



36

37: 75%
44: 17%

37: R^1 = H, R^2 = OH
44: R^1 = OH, R^2 = H

1-[1-Ethyl-3-(triisopropyl-silanyloxy)-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl]-2-hydroxy-propan-1-one (37): An anhydrous solution of triisopropylsilyl ether **36** (99.8 mg, 247 μmol, 1 equiv) in tetrahydrofuran (1050 μL + 2 × 250 μL) was added dropwise via cannula to a solution of potassium hexamethyldisilazane (KHMDS, 173 mg, 865 μmol, 3.50 equiv) in tetrahydrofuran (700 μL) at –78 °C. After the addition was complete, the reaction flask was placed on an ice-water bath for 5 min, and then moved to a dry ice-acetone bath at –78 °C for 5 min. A solution of (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine[8] (32.4 mg, 124 μmol, 0.500 equiv) in tetrahydrofuran (280 μL) was then added dropwise via syringe to the clear yellow reaction mixture. An additional four portions of (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine (4 × 8.05 mg, 30.9 μmol, 0.125 equiv) in tetrahydrofuran (70.0 μL) were added every 5 min and the progress of the reaction was monitored by TLC analysis after the addition of each portion. Five min after adding the last portion, ethyl acetate (3 mL) and a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (3:2, 3 mL) were added simultaneously, and the reaction flask was immediately removed from the dry ice-acetone bath. The mixture was diluted with additional portions of ethyl acetate (27 mL) and saturated aqueous sodium thiosulfate solution-satuated aqueous sodium bicarbonate solution (3:2, 22 mL) and the aqueous phase was separated from the yellow organic phase and extracted with ethyl acetate (3 × 22.5 mL). The combined organic phases were washed with a mixture of brine and saturated aqueous sodium thiosulfate solution (10:1, 15 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to ~500-μL volume. This crude sample was subjected to flash column chromatography on silica gel (eluent: 15% ethyl acetate in hexanes, diameter: 3.0 cm, height 25 cm) to afford the α-hydroxy ketones **37** (78.0 mg, 75%) and **44** (17.5 mg, 17%) as white powders.

α-Hydroxy Ketone 37:

^{1}H NMR (500 MHz, C_6D_6, 20°C): 5.47 (dq, *J* = 7.7, 6.7 Hz, 1H, C9–H), 5.13 (dd, *J* = 8.6, 5.9 Hz, 1H, C3–H), 4.10 (d, *J* = 7.8 Hz, 1H, C9-O**H**), 3.08 (dq, *J* = 13.9, 7.1 Hz, 1H, C11–H), 2.78 (dq, *J* = 13.9, 7.2 Hz, 1H, C11–H'), 2.64 (tdd, *J* = 11.0, 5.1, 3.4 Hz, 1H, C4a–H), 2.36 (ddd, *J* = 16.3, 6.3, 1.1 Hz, 1H, C7–H_c), 2.23 (dt, *J* = 11.2, 5.5 Hz, 1H, C4–H_c), 2.10 (ddd, *J* = 16.4, 12.1, 6.7 Hz, 1H, C7–H_t), 1.74 (td, *J* = 10.9, 8.6 Hz, 1H, C4–H_t), 1.57 (d, *J* = 6.7 Hz, 3H, C10–H), 1.49 (ddddd, *J* = 13.7, 6.7, 4.0, 2.8, 1.3 Hz, 1H, C6–H_t), 1.39 (t, *J* = 7.4 Hz, 3H, C12–H), 1.32 (dq, *J* = 12.5, 3.3 Hz, 1H, C5–H_c), 1.09–1.17 (m, 1H, C6–H_c), 1.09–1.17 (m, 21H, SiC**H**$(CH_3)_3$, SiCH$(CH_3)_3$), 0.74 (tdd, *J* = 12.7, 11.5, 2.6 Hz, 1H, C5–H_t).

[8] (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine was prepared from *N*-benzylidenebenzenesulfonamide according to the procedure of Ruano, J. L. G.; Aleman, J.; Fajardo, C.; Parra, A. *Org. Lett.* **2005**, *7*, 5493–5496. *N*-benzylidene-benzenesulfonamide was prepared according to the procedure of Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Syn.* **1988**, *66*, 203–210.

^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 201.2, 136.5, 127.5, 120.9, 115.5, 73.4, 71.6, 52.9, 46.3, 29.0, 24.7, 22.1, 20.0, 19.7, 18.8, 18.6, 16.5, 13.7.

FTIR (neat) cm^{-1}: 3459 (m, O–H), 2945 (s, C–H), 1643 (s, C=O), 1461 (m), 1117 (s).

HRMS–EI (*m*/*z*): calcd for $C_{24}H_{41}NO_3SiNa$ $[M + Na]^+$: 422.2748, found: 422.2761.

TLC (silica gel, 22.5% EtOAc–hexanes), *Rf*: 0.25 (UV, CAM).

α-Hydroxy Ketone 44:

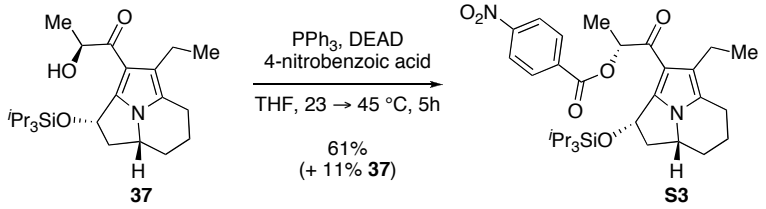
^{1}H NMR (500 MHz, C_6D_6, 20°C): 5.47 (dq, *J* = 7.2, 6.6 Hz, 1H, C9–H), 5.46 (dd, *J* = 7.8, 6.1 Hz, 1H, C3–H), 4.50 (d, *J* = 6.4 Hz, 1H, C9-O**H**), 3.11 (dq, *J* = 14.0, 7.1 Hz, 1H, C11–H), 2.86 (tdd, *J* = 10.7, 5.2, 3.6 Hz, 1H, C4a–H), 2.80 (dq, *J* = 13.9, 7.2 Hz, 1H, C11–H'), 2.40 (dt, *J* = 11.4, 5.7 Hz, 1H, C4–H_c), 2.33 (ddd, *J* = 16.5, 6.6, 1.1 Hz, 1H, C7–H_c), 2.08 (ddd, *J* = 16.6, 11.9, 6.9 Hz, 1H, C7–H_t), 1.74 (ddd, *J* = 11.2, 10.4, 8.0 Hz, 1H, C4–H_t), 1.56 (d, *J* = 6.9 Hz, 3H, C10–H), 1.49 (ddddd, *J* = 13.8, 6.9, 4.1, 2.7, 1.3 Hz, 1H, C6–H_t), 1.35 (t, *J* = 7.5 Hz, 3H, C12–H), 1.33–1.39 (m, 1H, C5–H_c), 1.07–1.15 (m, 1H, C6–H_c), 1.06–1.11 (m, 21H, SiC**H**$(CH_3)_3$, SiCH$(C\mathbf{H}_3)_3$), 0.75 (tdd, *J* = 12.9, 11.3, 2.6 Hz, 1H, C5–H_t).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 199.2, 138.2, 127.4, 120.9, 113.5, 73.3, 70.9, 53.7, 48.0, 29.5, 24.4, 21.9, 20.0, 19.8, 18.7, 18.6, 16.1, 13.6.

FTIR (neat) cm^{-1}: 3450 (m, O–H), 2944 (s, C–H), 1643 (s, C=O), 1462 (m), 1118 (s).

HRMS–EI (*m*/*z*): calcd for $C_{24}H_{41}NO_3SiNa$ $[M + Na]^+$: 442.2748, found: 442.2750.

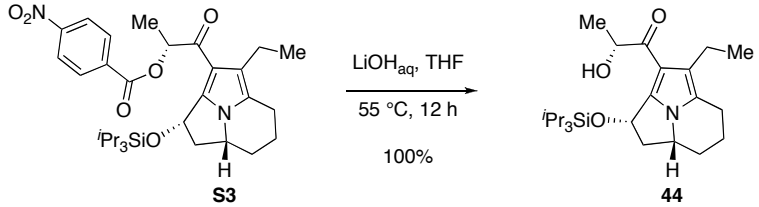
TLC (silica gel, 22.5% EtOAc–hexanes), *Rf*: 0.32 (UV, CAM).



4-Nitro-benzoic acid 2-[1-ethyl-3-(triisopropyl-silanyloxy)-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl]-1-methyl-2-oxo-ethyl ester (S3): Diethyl azodicarboxylate (DEAD, 150 μL, 952 μmol, 20.00 equiv) was added dropwise to a solution of triphenylphosphine (PPh_3, 300 mg, 114 μmol, 20.00 equiv) in tetrahydrofuran (600 μL) at 0 °C. The reaction flask was removed from the cooling bath and the resulting pale yellow solution was stirred for 5 min. This solution was drawn into a syringe and half of it (DEAD: 75.0 μL, 476 μmol, 10.00 equiv, PPh_3: 150 mg, 57.2 μmol, 12.00 equiv, tetrahydrofuran: 300 μL) was transferred to an anhydrous solution of α-hydroxy ketone **37** (20.0 mg, 47.6 μmol, 1 equiv) and 4-nitrobenzoic acid (79.5 mg, 476 μmol, 10.00 equiv) in tetrahydrofuran (600 μL) at 23 °C. The reaction flask was immediately placed on an oil bath at 45 °C. After 5h, the deep yellow solution was allowed to cool to room temperature and then diluted with ethyl acetate (15 mL), water (10 mL), and brine (1 mL). The aqueous phase was separated from the yellow organic phase and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated to a bright yellow residue. This residue was purified by flash column chromatography on silica gel (eluent: 9 → 12.5% ethyl acetate and 18 → 25% dichloromethane in hexanes, diameter: 2.5 cm, height: 22 cm) to afford the 4-nitrobenzoyl ester **S3** (16.4 mg, 61%) as a pale yellow oil, along with recovered α-hydroxy ketone **37** (3.1 mg, 11%).

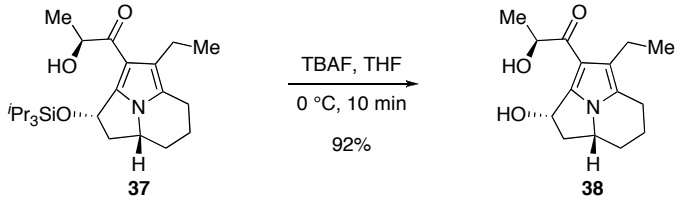
^{1}H NMR (500 MHz, C_6D_6, 20°C):	7.94 (d, *J* = 9.0 Hz, 2H, $NO_2CC\mathbf{H}$), 7.64 (d, *J* = 9.0 Hz, 2H, $NO_2CCHC\mathbf{H}$), 6.57 (q, *J* = 7.0 Hz, 1H, C9–H), 5.43 (dd, *J* = 8.3, 5.8 Hz, 1H, C3–H), 3.03 (dq, *J* = 13.9, 7.1 Hz, 1H, C11–H), 2.89 (dq, *J* = 13.9, 7.1 Hz, 1H, C11–H'), 2.84 (tdd, *J* = 10.9, 5.2, 3.9 Hz, 1H, C4a–H), 2.42 (dt, *J* = 11.1, 5.6 Hz, 1H, C4–H_c), 2.35 (ddd, *J* = 16.4, 6.4, 1.6 Hz, 1H, C7–H_c), 2.10 (ddd, *J* = 16.5, 12.1, 6.6 Hz, 1H, C7–H_t), 1.80 (td, *J* = 10.9, 8.4 Hz, 1H, C4–H_t), 1.72 (d, *J* = 6.9 Hz, 3H, C10–H), 1.50–1.56 (m, 1H, C6–H_t), 1.40 (t, *J* = 7.5 Hz, 3H, C12–H), 1.37–1.43 (m, 1H, C5–H_c), 1.07–1.18 (m, 1H, C6–H_c), 1.05–1.16 (m, 21H, $SiC\mathbf{H}(CH_3)_3$, $SiCH(C\mathbf{H}_3)_3$), 0.81 (tdd, *J* = 12.9, 11.3, 2.6 Hz, 1H, C5–H_t).
^{13}C NMR (125.8 MHz, C_6D_6, 20°C):	191.3, 164.4, 150.8, 137.5, 136.3, 131.2, 128.9, 127.7, 123.6, 120.8, 114.4, 75.8, 73.8, 53.3, 47.4, 29.4, 21.9, 20.3, 19.8, 19.2, 18.9, 18.8, 16.1, 13.9.
FTIR (neat) cm^{-1}:	2946 (m, C–H), 1728 (s, C=O), 1660 (s, C=O), 1529 (s), 1276 (s).
HRMS–EI (*m/z*):	calcd for $C_{31}H_{44}N_2O_6SiNa$ $[M + Na]^+$: 591.2861, found: 591.2867.

TLC (silica gel, 10% EtOAc, 20% CH_2Cl_2–hexanes), *Rf*: 0.42 (UV, CAM).



S3 44

1-[1-Ethyl-3-(triisopropyl-silanyloxy)-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl]-2-hydroxy-propan-1-one (44): Aqueous lithium hydroxide solution (LiOH, 3.5 M, 465 μL, 9.98 equiv) was added via syringe to a solution of 4-nitrobenzoyl ester **S3** (26.5 mg, 46.6 μmol, 1 equiv) in tetrahydrofuran (3.10 mL). The reaction flask was placed on an oil bath at 55 °C and the mixture was stirred vigorously, producing a finely dispersed suspension. After 12 h, the suspension was allowed to cool to room temperature then diluted with ethyl acetate (10 mL), water (6 mL), and brine (0.5 mL). The aqueous phase was separated and extracted with ethyl acetate (3 × 7.5 mL). The combined organic phases were washed with brine (5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to provide the α-hydroxy ketone **44** (19.6 mg, 100%) as an off-white solid. See the procedure on page S8 for characterization data.



37 38

1-(1-Ethyl-3-hydroxy-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl)-2-hydroxy-propan-1-one (38): Tetrabutylammonium fluoride (TBAF, 1.0 M in tetrahydrofuran, 270 μL, 270 μmol, 1.50 equiv) was added via syringe to a solution of α-hydroxy ketone **37** (75.2 mg, 179 μmol, 1 equiv) in tetrahydrofuran (3.60 mL) at 0 °C. After 10 min, chloroform (5 mL) and water (5 mL) were added simultaneously to the pale yellow solution and the reaction flask was immediately removed from the cooling bath. The mixture was diluted with additional portions of chloroform (7.5 mL) and brine (1.5 mL), and the aqueous phase was separated and extracted with chloroform (5 × 4 mL). The combined organic phases were washed with brine (5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to a pale yellow residue. This residue was purified by flash column chromatography on silica gel (eluent: 65 → 80% ethyl acetate in hexanes, diameter: 2.5 cm, height: 3.5 cm) to give the diol **38** (43.3 mg, 92%) as a white powder.

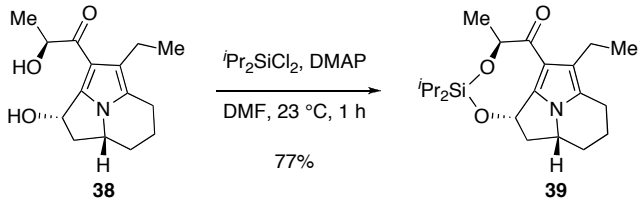
^{1}H NMR (500 MHz, $CDCl_3$, 20°C): 5.52 (s, 1H, C3-O**H**), 5.41 (dd, *J* = 7.9, 6.5 Hz, 1H, C3–H), 4.87 (pentet, *J* = 6.8 Hz, 1H, C9–H), 3.98 (d, *J* = 6.6 Hz, 1H, C9-O**H**), 3.92 (dddd, *J* = 11.3, 10.2, 5.4, 3.8 Hz, 1H, C4a–H), 3.05 (dt, *J* = 12.0, 6.0 Hz, 1H, C4–H_c), 2.79 (ddd, *J* = 16.5, 6.3, 1.1 Hz, 1H, C7–H_c), 2.58 (q, *J* = 7.6 Hz, 2H, C11–H), 2.52 (ddd, *J* = 16.6, 11.9, 6.4 Hz, 1H, C7–H_t), 2.15–2.22 (m, 2H, C5–H_c, C6–H_t), 2.12 (ddd, *J* = 12.0, 10.2, 8.1 Hz, 1H, C4–H_t), 1.76 (tddd, *J* = 14.2, 9.8, 5.1, 2.1 Hz, 1H, C6–H_c), 1.47 (dtd, *J* = 17.1, 12.7, 2.8 Hz, 1H, C5–H_t), 1.45 (d, *J* = 6.9 Hz, 3H, C10–H), 1.15 (t, *J* = 7.5 Hz, 3H, C12–H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20°C): 201.2, 144.6, 123.7, 122.5, 113.8, 70.6, 70.3, 56.2, 46.0, 29.9, 23.7, 22.3, 20.6, 20.1, 16.3.

FTIR (neat) cm^{-1}: 3358 (s, O–H), 2927 (s, C–H), 1638 (s, C=O), 1449 (s), 1089 (s).

HRMS–EI (*m/z*): calcd for $C_{15}H_{21}NO_3Na$ $[M + Na]^+$: 286.1414, found: 286.1421.

TLC (silica gel, 75% EtOAc–hexanes), *Rf*: 0.30 (UV, CAM).



[1,3,2]-Dioxasilocine ketone 39:

Diisopropyldichlorosilane (^{i}Pr$_2$SiCl$_2$, 44.5 μL, 247 μmol, 1.50 equiv) was added dropwise via syringe to a solution of diol **38** (43.3 mg, 164 μmol, 1 equiv) and 4-(dimethylamino)pyridine (DMAP, 70.1 mg, 574 μmol, 3.50 equiv) in dimethylformamide (DMF, 4.30 mL) at 23 °C. After 1 h, diethyl ether (17.5 mL) and a mixture of water and saturated aqueous sodium bicarbonate solution (3:1, 15 mL) were added and the aqueous phase was separated from the organic phase and extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine and 5% ethyl acetate in hexanes, diameter 3.0 cm, height 5.5 cm) to provide the diisopropylsilyl tethered diol **39** (47.8 mg, 77%) as a colourless oil.

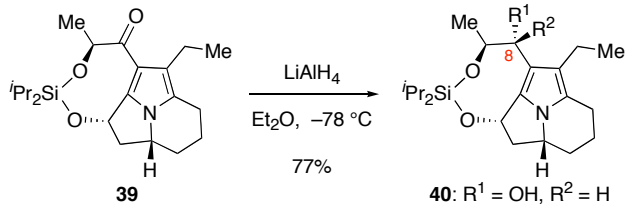
^{1}H NMR (500 MHz, C_6D_6, 20°C): 5.45 (dd, *J* = 8.5, 6.2 Hz, 1H, C3–H), 4.88 (q, *J* = 6.5 Hz, 1H, C9–H), 3.22 (dq, *J* = 13.9, 7.0 Hz, 1H, C11–H), 3.01 (dq, *J* = 13.8, 7.0 Hz, 1H, C11–H'), 2.92 (tdd, *J* = 10.9, 4.9, 3.7 Hz, 1H, C4a–H), 2.44 (ddd, *J* = 16.5, 6.5, 1.0 Hz, 1H, C7–H_c), 2.38 (dt, *J* = 11.5, 5.7 Hz, 1H, C4–H_c), 2.19 (ddd, *J* = 16.5, 12.0, 6.9 Hz, 1H, C7–H_t), 1.95 (ddd, *J* = 11.5, 10.7, 8.6 Hz, 1H, C4–H_t), 1.71 (d, *J* = 6.6 Hz, 3H, C10–H), 1.54 (t, *J* = 7.4 Hz, 3H, C12–H), 1.34–1.39 (m, 1H, C5–H_c), 1.51–1.57 (m, 1H, C6–H_t), 1.23–1.30 (m, 6H, SiCH(C**H**$_3$)$_3$), 1.14–1.18 (m, 3H, SiCH(C**H**$_3$)$_3$), 1.10–1.18 (m, 1H, C6–H_c), 1.10–1.14 (m, 3H, SiCH(C**H**$_3$)$_3$), 1.09–1.25 (m, 2H, SiC**H**(CH$_3$)$_3$), 0.76 (tdd, *J* = 12.5, 11.5, 2.7 Hz, 1H, C5–H_t).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 197.0, 137.9, 128, 120.7, 114.3, 76.1, 72.7, 53.4, 46.0, 29.4, 22.3, 22.1, 20.4, 20.0, 18.4, 18.2, 18.0, 17.9, 16.5, 12.9, 12.5.

FTIR (neat) cm^{-1}: 2946 (s), 1644 (s, C=O), 1463 (s), 1321 (s), 1119 (s).

HRMS–EI (*m/z*): calcd for $C_{21}H_{33}NO_3SiNa$ $[M + Na]^+$: 398.2122, found: 398.2128.

TLC (silica gel, 12.5% EtOAc–hexanes), *Rf*: 0.30 (UV, CAM).



39

40: R^1 = OH, R^2 = H
S4: R^1 = H, R^2 = OH

[1,3,2]-Dioxasilocine alcohol 40:

Lithium aluminum hydride (4.6 mg, 121 μmol, 7.00 equiv) was added as a solid in a single portion to a solution of diisopropylsilyl tethered diol **39** (6.5 mg, 17.3 μmol, 1 equiv) in diethyl ether (1.00 mL) at –78 °C and the reaction flask was immediately placed on an ice-water bath. After 15 min, saturated aqueous ammonium chloride solution (3 mL) was added, resulting in vigorous gas evolution. The reaction flask was immediately removed from the cooling bath and the reaction mixture was allowed to warm at room temperature. After 5 min, the mixture was diluted with ethyl acetate (6 mL), saturated aqueous ammonium chloride solution (2 mL), and water (1.5 mL). The opaque grey aqueous phase (pH 8) was separated and extracted with ethyl acetate (4 × 10 mL). The combined organic phases were washed with brine (3.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to a pale yellow residue. The crude dr was determined to be 10:1 by 1H NMR analysis. This crude residue was purified by flash column chromatography on silica gel (eluent: 1.5% triethylamine and 3 → 6% ethyl acetate in hexanes, diameter: 1.5 cm, height: 8.5 cm) to afford the azafulvenium ion precursors (5.0 mg, 77%). Two batches were obtained: one containing diastereomerically pure **40** (3.8 mg, 58%, >98:2 dr), along with a 1:1 mixture of C8 epimers **40** and **S4** (1.2 mg, 18%, 1:1 dr).

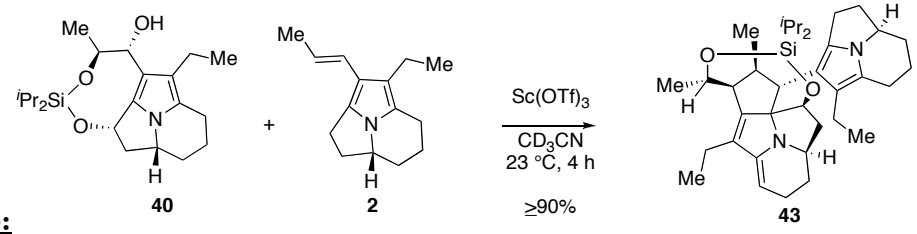
^{1}H NMR (500 MHz, C_6D_6, 20°C): 5.46 (dd, *J* = 8.8, 6.0 Hz, 1H, C3–H), 4.68 (qd, *J* = 6.5, 2.4 Hz, 1H, C9–H), 4.53 (dd, *J* = 4.5, 2.5 Hz, 1H, C8–H), 3.11 (tdd, *J* = 10.7, 4.6, 3.9 Hz, 1H, C4a–H), 2.50 (dq, *J* = 14.6, 7.4 Hz, 1H, C11–H), 2.48 (ddd, *J* = 16.2, 6.5, 1.0 Hz, 1H, C7–H$_c$), 2.44 (dq, *J* = 14.5, 7.3 Hz, 1H, C11–H'), 2.38 (ddd, *J* = 11.1, 6.1, 5.0 Hz, 1H, C4–H$_c$), 2.30 (ddd, *J* = 16.3, 11.7, 6.9 Hz, 1H, C7–H$_t$), 1.86 (ddd, *J* = 11.2, 10.4, 8.8 Hz, 1H, C4–H$_t$), 1.74 (heptet, *J* = 7.6 Hz, 1H, SiC**H**(CH$_3$)$_3$), 1.64 (d, *J* = 4.6 Hz, 1H, C8–O**H**), 1.58 (ddddd, *J* = 13.7, 6.9, 4.1, 2.7, 1.4 Hz, 1H, C6–H$_t$), 1.37 (dq, *J* = 12.5, 3.5 Hz, 1H, C5–H$_c$), 1.30–1.32 (m, 6H, C10–H, C12–H), 1.28–1.33 (m, 1H, SiC**H**(CH$_3$)$_3$), 1.28 (d, *J* = 7.6 Hz, 3H, SiCH(C**H**$_3$)$_3$), 1.26 (d, *J* = 7.6 Hz, 3H, SiCH(C**H**$_3$)$_3$), 1.18–1.30 (m, 1H, C6–H$_c$), 1.16–1.19 (m, 6H, SiCH(C**H**$_3$)$_3$), 0.79 (tdd, *J* = 12.9, 11.1, 2.4 Hz, 1H, C5–H$_t$).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 132.4, 123.4, 119.0, 113.7, 74.8, 71.6, 71.4, 53.9, 47.4, 29.9, 22.4, 21.5, 20.7, 19.3, 18.9, 18.8, 18.2, 18.2, 17.6, 13.9, 13.8.

FTIR (neat) cm^{-1}: 3588 (w, O–H), 2928 (s), 1436 (m), 1361 (m), 1094 (s).

HRMS–EI (*m*/*z*): calcd for $C_{21}H_{35}NO_3SiNa$ [M + Na]$^+$: 400.2278, found: 400.2265.

TLC (10% EtOAc–hexanes), *Rf*: 0.25 (CAM).



Heterodimer 43:

An anhydrous mixture of (+)-**2** (7.6 mg, 35.3 μmol, 2.00 equiv) and alcohol **40** (6.7 mg, 17.7 μmol, 1 equiv) was transferred in acetonitrile-d_3 (250 + 2 × 150 μL) to a sealed, argon-purged NMR tube. To this solution was added a solution of scandium trifluoromethanesulfonate (0.871 mg, 0.177 μmol, 0.100 equiv) in acetonitrile–d_3 (5.0 μL) via syringe, producing an intense yellow color. After 10 min, an additional portion of scandium trifluoromethanesulfonate (0.871 mg, 0.177 μmol, 0.100 equiv) in acetonitrile–d_3 (5.0 μL) was added, producing a white precipitate. After an additional 1h, four portions of scandium trifluoromethanesulfonate (0.435 mg, 0.177 μmol, 0.100 equiv) in acetonitrile–d_3 (2.5 μL) were added at 10 min intervals. When 1 h and 20 min had elapsed since the last portion of scandium trifluoromethanesulfonate had been added, ^{1}H NMR analysis showed clean and complete conversion to the desired and air-senstivie heterodimeric product (≥90%, ^{1}H NMR) with only remaining **2** (~45%, ^{1}H NMR). Triethylamine (5.0 μL, 35.4 μmol, 2.00 equiv) was added to the opaque, bright yellow sample, producing additional white precipitate. The mixture was then transferred under argon to a 5-mL pear-shaped flask, the transfer was completed with acetonitrile-d_3 (2 × 250 μL), and the suspension was concentrated under reduced pressure on an argon/high vacuum manifold (final volume approximately 150 μL). This deep orange suspension was immediately purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine and 2.5% ethyl acetate in hexanes, diameter: 1.5 cm, height: 4.0 cm) to yield the sensitive heterodimer **43** and co-eluting **2** (5:1) as a colorless oil that had to be rapidly secured for detailed analysis (including gCOSY, NOESY, and HSQC) due to sensitivity to oxidation.

^{1}H NMR (500 MHz, C_6D_6, 20°C): 4.74 (t, J = 6.2 Hz, 1H, C4–H), 4.65 (dd, J = 5.6, 3.7 Hz, 1H, C8–H), 4.48 (qd, J = 6.9, 1.4 Hz, 1H, C9–H), 3.32 (tdd, J = 10.7, 5.0, 3.7 Hz, 1H, C4a'–H), 3.18 (d, J = 8.5 Hz, 1H, C1–H), 3.11 (ddd, J = 13.8, 7.3, 6.4 Hz, 1H, C5a–H), 2.93 (ddd, J = 14.9, 11.1, 6.3 Hz, 1H, C3'–H$_c$), 2.52–2.80 (m, 6H, C11'–H, C11'–H', C3–H, C7'–H$_c$, C3'–H$_t$, C2–H), 2.45 (ddd, J = 16.1, 11.7, 6.5 Hz, 1H, C7'–H$_t$), 2.27 (dq, J = 14.4, 7.3 Hz, 1H, C11–H), 2.25 (dq, J = 14.3, 7.3 Hz, 1H, C11–H'), 2.01–2.14 (m, 4H, C5–H$_c$, C5–H$_t$, C7–H$_c$, C7–H$_t$), 1.84 (dq, J = 12.7, 6.3 Hz, 1H, C6–H$_c$), 1.59–1.71 (m, 2H, C6'–H$_t$, C4'–H$_t$), 1.56 (d, J = 7.3 Hz, 3H, C10'–H), 1.49–1.54 (m, 1H, C5'–H$_c$), 1.45 (d, J = 6.9 Hz, 3H, C10–H), 1.41–1.47 (m, 1H, C6–H$_t$), 1.41 (t, J = 7.5 Hz, 3H, C12'–H), 1.28–1.36 (m, 8H, SiC**H**(CH$_3$)$_3$, SiCH(C**H**$_3$)$_3$), 1.21 (t, J = 7.6 Hz, 3H, C12–H), 1.12–1.25 (m, 1H, C6'–H$_c$), 1.12–1.17 (m, 3H, SiCH(C**H**$_3$)$_3$), 0.88 (tdd, J = 13.3, 11.8, 3.0 Hz, 1H, C5'–H$_t$).

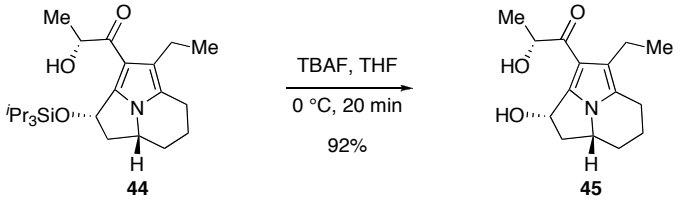
^{13}C NMR (125.8 MHz, C_6D_6, 20°C): 154.7, 148.5, 136.0, 126.0, 122.4, 119.3, 113.5, 90.2, 89.8, 86.7, 73.4, 55.3, 55.3, 53.3, 49.4, 47.0, 41.4, 37.2,

30.8, 30.2, 27.4, 26.2, 24.6, 23.1, 21.1, 21.0, 19.7, 18.9, 18.6, 18.4, 18.3, 18.1, 17.0, 14.2, 12.8, 12.1.

FTIR (neat) cm^{-1}: 2940 (s), 1730 (m), 1668 (m), 1461 (m), 1095 (m).

HRMS–EI (*m/z*): calcd for $C_{36}H_{55}N_2O_2Si$ $[M + H]^+$: 575.4027, found: 575.4043.

TLC (Et_3N–pretreated silica, 2.5% Et_3N, 2.5% EtOAc–hexanes), *Rf*: 0.76 (UV, CAM).



44 **45**

1-(1-Ethyl-3-hydroxy-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl)-2-hydroxy-propan-1-one (45): Tetrabutylammonium fluoride (1.0 M in THF, 100 μL, 100 μmol, 1.67 equiv) was added via syringe to a solution of triisopropylsilyl ether **44** (24.9 mg, 59.3 μmol, 1 equiv) in tetrahydrofuran (2.00 mL) at 0 °C. After 20 min, chloroform (5 mL) and aqueous sodium chloride solution (10 wt%, 5 mL) were added simultaneously to the pale yellow solution and the reaction flask was immediately removed from the cooling bath. The mixture was diluted with additional portions of chloroform (10 mL) and aqueous sodium chloride solution (10 wt%, 5 mL). The aqueous layer was separated and extracted with chloroform (5 × 10 mL), and the combined organic layers were washed with brine (7.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to a pale yellow solution in chloroform (150 μL). This crude solution was purified by flash column chromatography on silica gel (eluent: 65 → 80% ethyl acetate in hexanes, diameter: 2.5 cm, height: 3.5 cm) to provide the diol **45** (14.4 mg, 92%) as a white powder.

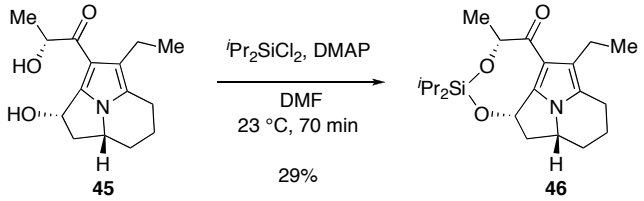
^1H NMR (500 MHz, $CDCl_3$, 20°C): 5.46 (dd, *J* = 8.2, 6.4 Hz, 1H, C3–H), 4.97 (q, *J* = 6.5 Hz, 1H, C9–H), 4.09 (br s, 1H, C9-O**H**), 3.90 (dddd, *J* = 11.3, 10.1, 5.2, 3.6 Hz, 1H, C4a–H), 3.08 (ddd, *J* = 11.9, 6.4, 5.5 Hz, 1H, C4–H_c), 2.97 (br s, 1H, C3–O**H**), 2.78 (ddd, *J* = 16.7, 6.7, 1.1 Hz, 1H, C7–H_c), 2.66 (dq, *J* = 14.5, 7.3 Hz, 1H, C11–H), 2.58 (dq, *J* = 14.4, 7.2 Hz, 1H, C11–H'), 2.56 (ddd, *J* = 16.2, 11.8, 6.5 Hz, 1H, C7–H_t), 2.15–2.22 (m, 2H, C5–H_c, C6–H_t), 2.05 (ddd, *J* = 12.0, 10.2, 8.3 Hz, 1H, C4–H_t), 1.71–1.83 (m, 1H, C6–H_c), 1.43 (d, *J* = 6.7 Hz, 3H, C10–H), 1.37–1.49 (m, 1H, C5–H_t), 1.17 (t, *J* = 7.5 Hz, 3H, C12–H).

^{13}C NMR (125.8 MHz, $CDCl_3$, 20°C): 199.6, 142.3, 125.4, 122.3, 113.4, 71.0, 70.6, 55.5, 46.8, 29.8, 23.5, 22.2, 20.3, 20.0, 16.5.

FTIR (neat) cm^{-1}: 3331 (s, O–H), 2929 (s, C–H), 1635 (s, C=O), 1448 (s), 1092 (s).

HRMS–EI (*m/z*): calcd for $C_{15}H_{21}NO_3Na$ $[M + Na]^+$: 286.1414, found: 286.1424.

TLC (silica gel, 65% EtOAc–hexanes), *Rf*: 0.20 (UV, CAM).

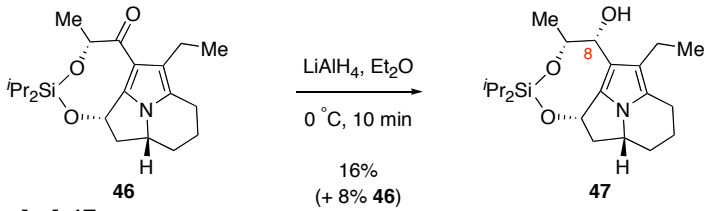


[1,3,2]-Dioxasilocine ketone 46:

Diisopropyldichlorosilane (^{i}Pr$_2$SiCl$_2$, 13.6 μL, 75.2 μmol, 1.50 equiv) was added dropwise via syringe to a solution of diol **45** (13.2 mg, 50.1 μmol, 1 equiv) and 4-(dimethylamino)pyridine (21.4 mg, 175 μmol, 3.50 equiv) in dimethylformamide (1.00 mL) at 23 °C, producing a white suspension. Additional portions of diisopropyldichlorosilane (6.8 μL, 37.7μmol, 0.750 equiv) and 4-(dimethylamino)pyridine (21.4 mg, 75.2 μmol, 3.50 equiv) were added after 25 min and 55 min, respectively. After 70 min total reaction time, TLC analysis indicated that the starting material had been completely consumed. Diethyl ether (10 mL) and a mixture of water and saturated aqueous sodium bicarbonate solution (7:1, 8 mL) were added. The aqueous layer was separated and extracted with ethyl acetate (3 × 7.5 mL). The combined organic phases were washed with brine (6 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. This residue was purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine and 2 → 75% ethyl acetate in hexanes, diameter 1.5 cm, height 22 cm) to afford the diisopropylsilyl tethered diol **46** (5.5 mg, 29%) as a colorless oil. The remainder of the material isolated from the column, consisting of a mixture of C3 and C9 mono- and bis-silylated byproducts, was combined and diol **45** was recovered by their treatment with tetrabutylammonium fluoride in tetrahydrofuran at 0°C.

^{1}H NMR (500 MHz, C_6D_6, 20°C):	5.29 (dd, *J* = 7.5, 6.6 Hz, 1H, C3–H), 4.90 (q, *J* = 6.2 Hz, 1H, C9–H), 3.08 (dq, *J* = 13.8, 7.1 Hz, 1H, C11–H), 2.94 (dq, *J* = 13.8, 7.1 Hz, 1H, C11–H'), 2.83 (tdd, *J* = 10.8, 5.9, 3.5 Hz, 1H, C4a–H), 2.47 (dt, *J* = 12.1, 6.1 Hz, 1H, C4–H_c), 2.30 (ddd, *J* = 16.4, 6.6, 1.1 Hz, 1H, C7–H_c), 2.06 (ddd, *J* = 16.5, 12.0, 6.9 Hz, 1H, C7–H_t), 1.79 (ddd, *J* = 12.1, 10.4, 7.6 Hz, 1H, C4–H_t), 1.66 (d, *J* = 6.3 Hz, 3H, C10–H), 1.48 (ddddd, *J* = 13.7, 6.9, 4.0, 2.7, 1.4 Hz, 1H, C6–H_t), 1.40 (t, *J* = 7.5 Hz, 3H, C12–H), 1.36 (dq, *J* = 12.5, 3.4 Hz, 1H, C5–H_c), 1.16 (d, *J* = 7.1 Hz, 3H, SiCH(C**H**$_3$)$_3$), 1.13 (d, *J* = 7.0 Hz, 3H, SiCH(C**H**$_3$)$_3$), 1.05–1.12 (m, 1H, C6–H_c), 1.16 (d, *J* = 7.1 Hz, 3H, SiCH(C**H**$_3$)$_3$), 1.04–1.21 (m, 1H, SiC**H**(CH$_3$)$_3$), 0.90 (d, *J* = 7.2 Hz, 3H, SiCH(C**H**$_3$)$_3$), 0.87 (d, *J* = 7.1 Hz, 3H, SiCH(C**H**$_3$)$_3$), 0.77–0.81 (m, 1H, C5–H_t), 0.76–0.86 (m, 1H, SiC**H**(CH$_3$)$_3$).
^{13}C NMR (125.8 MHz, C_6D_6, 20°C):	192.4, 136.4, 128.9, 121.0, 115.8, 72.5, 71.6, 53.3, 47.3, 29.6, 22.2, 19.9, 19.7, 18.6, 17.8, 17.7, 17.6, 17.4, 16.1, 13.5, 13.3.
FTIR (neat) cm^{-1}:	2931 (s), 2866 (s), 1666 (s, C=O), 1445 (m) , 1110 (s).
HRMS–EI (*m/z*):	calcd for $C_{21}H_{33}NO_3SiNa$ [M + Na]$^+$: 398.2122, found: 398.2112.

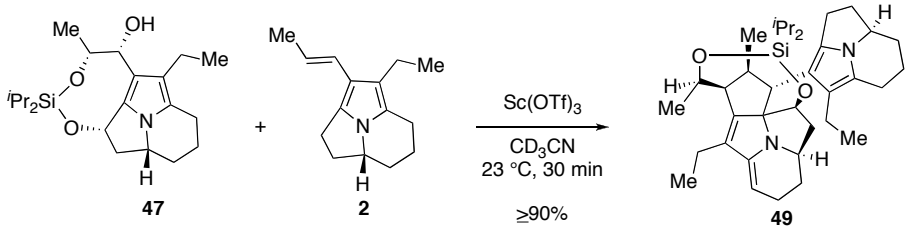
TLC (silica gel, 12.5% EtOAc–hexanes), *Rf*: 0.22 (UV, CAM).



[1,3,2]-Dioxasilocine alcohol 47:

Lithium aluminum hydride (11.9 mg, 313 μmol, 10.00 equiv) was added as a solid in a single portion to a solution of ketone **46** (11.8 mg, 31.3 μmol, 1 equiv) in diethyl ether (Et_2O, 1.60 mL) at 0 °C. After 10 min, the mixture was diluted with saturated aqueous ammonium chloride solution (4 mL) and ethyl acetate (3 mL), and the reaction flask was immediately removed from the cooling bath. The reaction mixture was stirred at room temperature for 5 min, then diluted with additional portions of ethyl acetate (50 mL) and saturated aqueous ammonium chloride solution (50 mL). The opaque grey aqueous phase (pH 7) was separated and extracted with ethyl acetate (4 × 40 mL). The combined organic phases were washed with brine (35 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The white residue was purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine and 5% ethyl acetate in hexanes changed gradually to 2.5% triethylamine and 3.5% methanol in ethyl acetate, diameter: 1.5 cm, height: 10 cm) to afford the sensitive alcohol **47** (1.9 mg, 16%) as a colorless oil. The remainder of the material isolated from the column consisted of recovered starting material (1.0 mg, 8.4%) and the fully desilylated C3-C8-C9 triol (2.9 mg, 24%).

^{1}H NMR (500 MHz, C_6D_6, 20°C):	5.25 (dd, *J* = 7.3, 6.7 Hz, 1H, C3–H), 4.60 (d, *J* = 11.4 Hz, 1H, C8–H), 4.48 (q, *J* = 6.3 Hz, 1H, C9–H), 3.03 (tdd, *J* = 10.8, 5.4, 3.2 Hz, 1H, C4a–H), 2.97 (dq, *J* = 14.7, 7.6 Hz, 1H, C11–H), 2.74 (dq, *J* = 14.3, 7.3 Hz, 1H, C11–H'), 2.51 (ddd, *J* = 11.7, 6.3, 5.5 Hz, 1H, C4–H_c), 2.49 (d, *J* = 11.4 Hz, 1H, C8–O**H**), 2.48 (ddd, *J* = 16.3, 6.7, 1.3 Hz, 1H, C7–H_c), 2.27 (ddd, *J* = 16.3, 11.9, 6.8 Hz, 1H, C7–H_t), 1.91 (ddd, *J* = 11.7, 10.6, 7.5 Hz, 1H, C4–H_t), 1.59 (ddddd, *J* = 13.7, 6.8, 4.0, 2.7, 1.4 Hz, 1H, C6–H_t), 1.46 (d, *J* = 6.3 Hz, 3H, C10–H), 1.42–1.46 (m, 1H, C5–H_c), 1.40 (t, *J* = 7.5 Hz, 3H, C12–H), 1.23 (tddd, *J* = 13.4, 12.1, 6.5, 3.0 Hz, 1H, C6–H_c), 1.12–1.15 (m, 6H, SiCH(C**H**$_3$)$_3$), 1.06–1.15 (m, 1H, SiC**H**$(CH_3)_3$), 0.98 (d, *J* = 7.1 Hz, 3H, SiCH(C**H**$_3$)$_3$), 0.85–0.91 (m, 1H, C5–H_t), 0.82–0.95 (m, 1H, SiC**H**$(CH_3)_3$).
^{13}C NMR (125.8 MHz, C_6D_6, 20°C):	128, 125.2, 119.4, 118.0, 71.5, 71.1, 70.8, 52.7, 47.4, 29.8, 22.8, 22.6, 20.6, 19.4, 18.1, 18.0, 18.0, 17.8, 16.6, 12.8, 12.4.
HRMS–EI (*m*/*z*):	calcd for $C_{21}H_{35}NO_3SiNa$ $[M + Na]^+$: 400.2278, found: 400.2281.
TLC (silica gel, 10% EtOAc–hexanes), *Rf*:	0.36 (CAM).



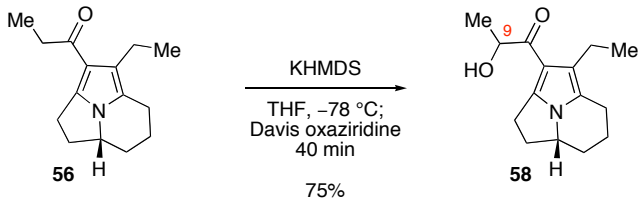
Heterodimer 49:

An anhydrous solution of (+)-myrmicarin 215B (**2**, 1.1 mg, 5.01 μmol, 1.00 equiv) in acetonitrile–d_3 (500 μL) was added portionwise to an anhydrous solution of alcohol **47** (1.9 mg, 5.01 μmol, 1 equiv) in acetonitrile–d_3 (250 μL) until ^{1}H NMR analysis showed that the ratio of the two species was exactly 1:1. This solution was concentrated (final volume 150 μL) and transferred under argon to a sealed, argon-purged NMR tube, followed by an acetonitrile–d_3 (2 × 30 μL) rinse of the transfer flask. To this solution, scandium trifluoromethanesulfonate (0.246 mg, 0.501 μmol, 0.100 equiv) in acetonitrile–d_3 (5.0 μL) was added via syringe, producing an intense yellow color. After 10 min, an additional two portions of scandium trifluoromethanesulfonate (2 × 0.246 mg, 0.501μmol, 0.100 equiv) were added at 10 min intervals. When 10 min had elapsed since the last portion of scandium trifluoromethanesulfonate was added, ^{1}H NMR analysis showed complete and clean formation of the desired heterodimer **49** (≥90%) as a single diastereomer and trace amount of remaining **2** (<5%). Triethylamine (5.0 μL, 35.9 μmol, 7.16 equiv) was added to the intense yellow solution, producing a small amount of precipitate. The sample was transferred under argon to a 5-mL pear-shaped flask, the NMR tube was rinsed with acetonitrile–d_3 (2 × 100 μL), and the suspension was concentrated under reduced pressure on an argon/high vacuum manifold (final volume ~200 μL). This sample was directly purified by flash column chromatography on a silica gel (eluent: 2.5% triethylamine and 2.5% ethyl acetate in hexanes, diameter: 1.0 cm, height: 2.5 cm) to afford the sensitive heterodimer **49** and myrmicarin 215B (>95:5) as a colorless oil that had to be rapidly secured for detailed analysis (including gCOSY, gHSQC, NOESY, and gHMBC) due to sensitivity to oxidation.

^{1}H NMR (500 MHz, C_6D_6, 23°C): 4.66 (dd, J = 7.5, 3.0 Hz, 1H, C8–H), 4.28 (d, J = 4.3 Hz, 1H, C4–H), 4.11 (qd, J = 8.9, 5.8 Hz, 1H, C9–H), 3.30 (tdd, J = 10.6, 5.3, 3.5 Hz, 1H, C4a'–H), 3.18 (dddd, J = 11.6, 9.3, 6.4, 2.1 Hz, 1H, C5a–H), 2.95 (ddd, J = 15.2, 11.1, 6.2 Hz, 1H, C3'–H_c), 2.56–2.71 (m, 5H, C3–H, C7'–H_c, C3'–H_t, C11'–H, C11'–H'), 2.53 (d, J = 9.0 Hz, 1H, C1–H), 2.45 (dq, J = 14.6, 7.4 Hz, 1H, C11–H), 2.31–2.49 (m, 3H, C7–H_t, C5–H_c, C2–H), 2.27 (dq, J = 14.6, 7.4 Hz, 1H, C11–H'), 2.16 (ddt, J = 15.2, 11.9, 3.3 Hz, 1H, C7–H_t), 2.06 (dt, J = 11.4, 5.9 Hz, 1H, C4'–H_c), 2.04–2.12 (m, 1H, C2–H), 1.95 (dd, J = 13.7, 1.8 Hz, 1H, C5–H_t), 1.56–1.68 (m, 3H, C6'–H_t, C4'–H_t, C6–H_c), 1.51 (td, J = 11.8, 4.0 Hz, 1H, C6–H_t), 1.42–1.48 (m, 1H, C5'–H_c), 1.35 (t, J = 7.5 Hz, 3H, C12'–H), 1.32 (d, J = 5.8 Hz, 3H, C10–H), 1.27 (t, J = 7.5 Hz, 3H, C12–H), 1.24–1.32 (m, 2H, C6'–H_c, SiC**H**$(CH_3)_3$), 1.17 (d, J = 7.4 Hz, 3H, SiCH(C**H**$_3)_3$), 1.14 (d, J = 7.4 Hz,

	3H, SiCH(C**H**$_3$)$_3$), 1.09–1.14 (m, 6H, SiCH(C**H**$_3$)$_3$), 1.08–1.18 (m, 1H, SiC**H**(CH$_3$)$_3$), 0.99 (d, J = 7.0 Hz, 3H, C10'–H), 0.82 (tdd, J = 13.1, 11.7, 3.3 Hz, 1H, C5'–H$_t$).
^{13}C NMR (125.8 MHz, C_6D_6, 23°C):	154.3 (C8a), 145.9 (C3a), 134.1 (C8b), 131.2 (C2a'), 121.9 (C1'), 116.8 (C7a'), 113.4 (C2'), 91.4 (C3b), 87.1 (C8), 84.7 (C4), 67.7 (C9), 55.3 (C4a'), 55.0 (C5a), 50.2 (C3), 49.7 (C2), 48.2 (C1), 43.5 (C5), 37.2 (C4'), 31.1 (C6), 30.1 (C5'), 27.4 (C3'), 25.9 (C10), 23.3 (C7), 23.2 (C6'), 21.3 (C7), 19.6 (C11), 19.2 (C11'), 18.6 (SiCH(**C**H$_3$)$_3$), 18.5 (SiCH(**C**H$_3$)$_3$, 18.2 (SiCH(**C**H$_3$)$_3$, 18.2 (SiCH(**C**H$_3$)$_3$, 17.8 (C12'), 17.3 (C10'), 14.3 (C12), 12.1 (Si**C**H(CH$_3$)$_3$, 11.5 (Si**C**H(CH$_3$)$_3$.
FTIR (neat) cm^{-1}:	2929 (s), 1717 (m), 1653 (m), 1507 (w), 1118 (m).
HRMS–EI (m/z):	calcd for $C_{36}H_{55}N_2O_2Si$ [M + H]$^+$: 575.4027, found: 575.4033.

TLC (Et_3N–pretreated silica, 2.5% Et_3N, 2.5% EtOAc–hexanes), Rf: 0.82 (UV, CAM).



1-(1-Ethyl-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl)-2-hydroxy-propan-1-one (58):

An anhydrous solution of ketone **56** (97.3 mg, 421 μmol, 1 equiv) in tetrahydrofuran (2500 + 2 × 250 μL) was added via cannula to a solution of potassium bis(trimethylsilyl)amide (KHMDS, 209 mg, 1.05 mmol, 2.50 equiv) in tetrahydrofuran (750 μL) at –78 °C , producing a clear and pale yellow solution. After 15 min, a solution of (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine[8] (110 mg, 421 μmol, 1.00 equiv) in tetrahydrofuran (440 μL) was added dropwise via syringe. After 5 min, two additional portions of (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine (11.0 mg, 42.1 μmol, 0.100 equiv) in tetrahydrofuran (44.0 μL) were added at 5 min intervals. When 5 min had elapsed after the last addition, a mixture of saturated aqueous sodium thiosulfate solution and saturated aqueous sodium bicarbonate solution (1:1, 3 mL) was added to the yellow reaction mixture and the reaction flask was immediately removed from the cooling bath. The mixture was diluted with ethyl acetate (20 mL) and an additional portion of saturated aqueous sodium thiosulfate solution-saturated aqueous sodium bicarbonate solution (1:1, 12 mL), and the aqueous phase was extracted with ethyl acetate (4 × 15 mL). The combined organic phases were washed with brine (12.5 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to a yellow solution in ethyl acetate (approximately 300 μL). This sample was directly purified by flash column chromatography on silica gel (eluent: 2.5% triethylamine, 37.5% ethyl acetate, and 15%

dichloromethane in hexanes, diameter: 2.5 cm, height: 17 cm) to afford the α-hydroxy ketone **58** (78.0 mg, 75%, mixture of C9 epimers, 9:5 dr) as a while powder.

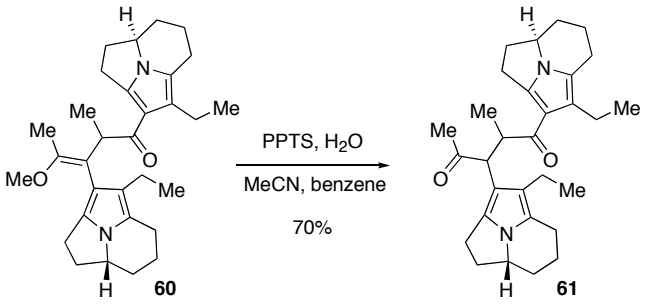
^{1}H NMR (500 MHz, C_6D_6, 20°C, 9:5 dr, major epimer denoted by *): 4.67–4.78 (m, 2H, C9–H*, C9–H), 4.55–4.57 (m, 2H, C9–O**H***, C9–O**H**), 2.85–3.17 (m, 6H, C11–H*, C11–H'*, C11–H, C11–H', C4a–H*, C4a–H), 2.04–2.42 (m, 8H, C3–H_t*, C3–H_t, C7–H_c*, C7–H_c, C3–H_c*, C3–H_c, C7–H_t*, C7–H_t), 1.65–1.71 (m, 2H, C4–H_c*, C4–H_c), 1.47–1.56 (m, 2H, C6–H_t*, C6–H_t), 1.42–1.46 (m, 12H, C12–H*, C12–H, C10–H*, C10–H), 1.19–1.39 (m, 4H, C4–H_t*, C4–H_t, C5–H_c*, C5–H_c), 1.07–1.18 (m, 2H, C6–H_c*, C6–H_c), 0.59–0.69 (C5–H_t*, C5–H_t*).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C, 9:5 dr, major epimer denoted by *): 197.3*, 197.2, 138.1, 138.1*, 126.7*, 126.5, 121.7, 121.5*, 113.3, 113.2*, 70.5, 70.1*, 56.1*, 56.0, 36.3, 35.9*, 29.5, 29.4*, 28.3, 28.0*, 23.9*, 23.8, 22.6*, 22.3, 20.1, 20.1*, 19.9*, 19.8, 16.3*, 16.1.

FTIR (neat) cm^{-1}: 3451 (m, O–H), 2921 (s), 1632 (s, C=O), 1460 (m), 1370 (m), 1039 (m).

HRMS–EI (*m*/*z*): calcd for $C_{15}H_{21}NO_2Na$ $[M + Na]^+$: 270.1465, found: 270.1469.

TLC (2.5% Et_3N, 17.5% EtOAc, 20% CH_2Cl_2–hexanes), *Rf*: 0.21 (UV, CAM).



1,3-Bis-(1-ethyl-3,4,4a,5,6,7-hexahydro-pyrrolo[2,1,5-*cd*]indolizin-2-yl)-2-methyl-pentan-1,4-dione (61):

To a degassed solution (argon purge, 15 min) of methyl ether **60** (140 mg, 304 μmol, 1 equiv) in benzene (10.0 mL) was added a degassed solution (argon purge, 15 min) of pyridinium *p*-toluenesulfonic acid (PPTS, 115 mg, 456 μmol, 1.50 equiv) and deionized water (H_2O, 15.0 μL, 832 μmol, 2.74 equiv) in acetonitrile (1.00 mL). The resulting deep orange fine suspension was sonicated for 30 min, then saturated aqueous sodium bicarbonate solution (15 mL) was added and the mixture was diluted with ethyl acetate (25 mL). The aqueous phase was separated and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (12.5 mL) and were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The red residue was purified by flash column chromatography on silica gel (eluent: 1% triethylamine and 17.5 → 35% ethyl acetate in hexanes, diameter: 2.5 cm, height: 24 cm) to provide the air-sensitive diketone **61** (94.5 mg, 70%, nearly equal mixture of stereoisomers) as an off-white solid.

^{1}H NMR (500 MHz, C_6D_6, 20°C, mixture of 4 stereoisomers, 1.20:1:1.20:1.22 dr): 4.62 (d, *J* = 10.9 Hz, 1H, C3–H), 4.56 (d, *J* = 10.5 Hz, 1H, C3–H), 4.46 (d, *J* = 10.4 Hz, 1H, C3–H), 4.38 (d, *J* = 10.4 Hz, 1H, C3–H), 3.95–4.14 (m, 4H), 1.80–3.50 (m, 64H), 2.16 (s, 3H, C10–H), 2.11 (s, 3H, C10–H), 2.08 (s, 3H, C10–H), 2.02 (s, 3H, C10–H), 1.20–1.70 (m, 60H), 0.54–1.18 (m, 16H).

^{13}C NMR (125.8 MHz, C_6D_6, 20°C, mixture of 4 stereoisomers, 1.20:1:1.20:1.22 dr): 207.8, 207.2, 206.4, 206.3, 200.0, 199.9, 198.1, 198.0, 137.4, 137.4, 136.8, 136.7, 129.3, 129.0, 128.9, 128.0, 126.4, 126.2, 126.2, 125.8, 122.8, 122.6, 122.2, 122.2, 120.9, 120.8, 120.8, 120.7, 119.4, 119.4, 119.3, 119.1, 118.0, 117.4, 117.0, 116.8, 110.8, 110.3, 109.8, 109.4, 56.0, 55.9, 55.9, 55.9, 55.6, 55.4, 55.4, 55.2, 53.1, 52.6, 52.4, 52.4, 46.6, 46.2, 46.0, 45.2, 37.4, 37.4, 37.3, 37.3, 36.7, 36.2, 36.1, 36.0, 30.6, 30.4, 30.1, 30.0, 30.0, 29.9, 29.7, 29.7, 29.6, 29.5, 28.7, 28.6, 28.4, 28.4, 26.5, 25.7, 23.1, 23.1, 23.1, 22.9, 22.9, 22.8, 22.7, 22.7, 22.5, 21.1, 21.0, 21.0, 21.0, 20.3, 20.2, 20.1, 20.1, 20.1, 19.9, 19.9, 19.9, 19.2,

	19.2, 19.0, 19.0, 18.9, 18.7, 18.5, 18.0, 17.8, 17.1, 17.0, 16.7, 16.7, 16.4, 16.4, 16.4, 16.3, 16.2, 16.2.
FTIR (neat) cm^{-1}:	2928 (s, C–H), 1706 (s, C=O), 1641 (s, C=O), 1497 (s), 1428 (s), 1321 (s), 1167 (m).
HRMS–EI (*m/z*):	calcd for $C_{30}H_{41}N_2O_2$ $[M + H]^+$: 461.3163, found: 461.3149.

TLC (1% Et_3N, 20% EtOAc–hexanes), *Rf*: 0.33 (UV, CAM).

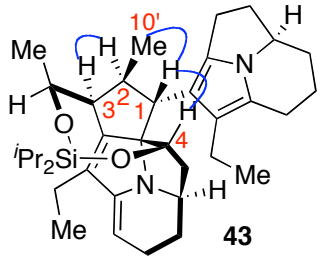
NOESY Correlations for heterodimers **43** and **49**.

Proton signal	NOESY correlations	
	43	**49**
C1–H	C4–H, C10'–CH_3, C11'-CH_2	C4–H, C9–H, C10'–CH_3
C2–H	C3–H, C10'–CH_3	C3–H, C10'–CH_3
C3–H	C2–H, C9–H, C10–CH_3	C2–H, C10–CH_3, C12–CH_3
C4–H	C1–H, C5a–H, C5–H_c/C5–H_t	C1–H, C5–H_c, C9–H
C5–H_c	C4–H, C5a–H[a]	C4–H, C5a–H, C5–H_t
C5–H_t		C4–H, C5–H_t, C6–H_t
C5a–H	C4–H, C5–H_c/C5–H_t	C5–H_c, C6–H_c
C6–H_c	C5a–H, C6–H_t, C7–H_c/C7–H_t	C5a–H, C6–H_t, C7–H_c
C6–H_t	C6–H_c, C7–H_c/C7–H_t	C5–H_t, C6–H_c, C7–H_t
C7–H_c	C6–H_c, C6–H_t, C8–H[b]	C6–H_c, C7–H_t, C8–H
C7–H_t		C6–H_t, C7–H_c
C8–H	C7–H_c/C7–H_t, C11–H	C7–H_c, C11–CH_2, C12–CH_3
C9–H	C3–H, C10–CH_3	C1–H, C4–H, C10–CH_3, C10'–CH_3
C10–CH_3	C3–H, C9–H	C3–H, C9–H, C10'–CH_3
C11–H	C8–H, C12–CH_3	C8–H, C12–CH_3[c]
C11–H'	C12–CH_3	
C12–CH_3	C11–H	C3–H, C11–CH_2
C10'–CH_3	C1–H, C2–H	C1–H, C2–H, C10–CH_3
C3'–H_c	C3'–H_t, C4'–H_c	C3'–H_t, C4'–H_c
C3'–H_t	C3'–H_c, C4'–H_t	C3'–H_c, C4'–H_t
C4'–H_c	C3'–H_c, C4'–H_t, C4a'–H	C3'–H_c, C4a'–H, C4'–H_t
C4'–H_t	C3'–H_t, C4'–H_c	C3'–H_t, C4'–H_c
C4a'–H	C4'–H_c, C5'–H_c, C6'–H_c	C4'–H_c, C5'–H_c, C6'–H_c
C5'–H_c	C4a'–H, C6'–H_c, C6'–H_t	C4a'–H, C6'–H_t
C5'–H_t	C5'–H_c, C6'–H_t	C5'–H_c, C6'–H_t
C6'–H_c	C4a'–H, C6'–H_t, C7'–H_c	C4a'–H, C6'–H_t, C7'–H_c
C6'–H_t	C6'–H_c, C7'–H_t	C5'–H_c, C5'–H_t, C6'–H_c, C7'–H_t
C7'–H_c	C6'–H_c, C7'–H_t	C6'–H_c, C6'–H_t, 7't
C7'–H_t	C6'–H_t, C7'–H_c	C7'–H_c
C11'–CH_2	C1–H, C12'–CH_3	C12'–CH_3
C12'–CH_3	C11'–CH_2	C11'–CH_2

[a]Signals for protons C5–H_c and C5–H_t overlap in the ^{1}H NMR spectrum of **43**. [b]Signals for protons C7–H_c and C7–H_t overlap in the ^{1}H NMR spectrum of **43**. [c]Signals for protons C11–H and C11–H' overlap in the ^{1}H NMR spectrum of **49**.

Summary of key correlations:

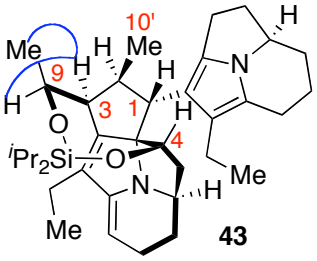
Key correlations for assignment of C1, C2, C3 stereochemistry of heterodimer **43**:



43

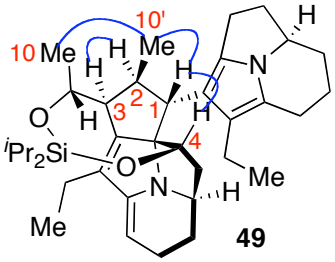
Key correlations for assignment of C9 stereochemistry of heterodimer **43**:

no C9–H/C10'–CH$_3$ correlation



43

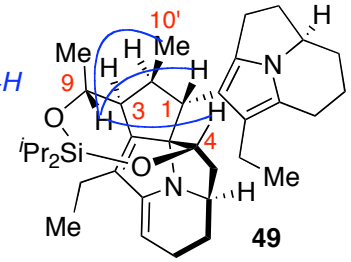
Key correlations for assignment of C1, C2, C3 stereochemistry of heterodimer **49**:



49

Key correlations for assignment of C9 stereochemistry of heterodimer **49**:

no C3–H/C9–H correlation



49

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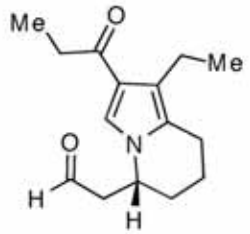
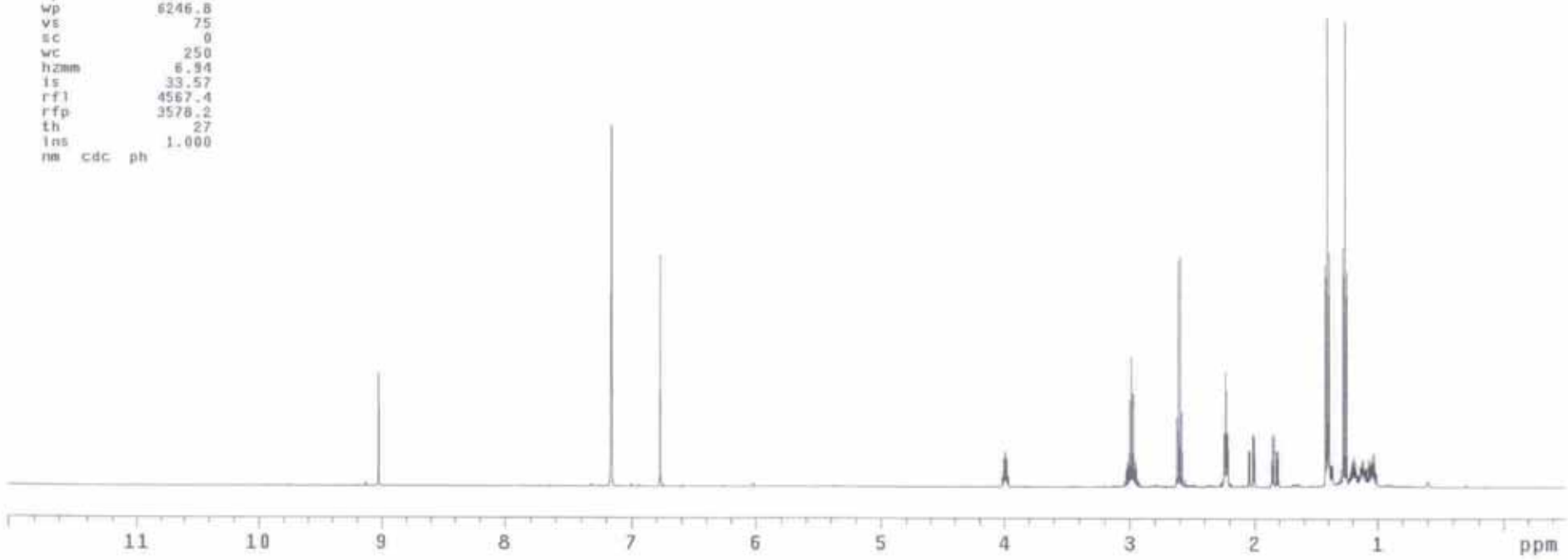
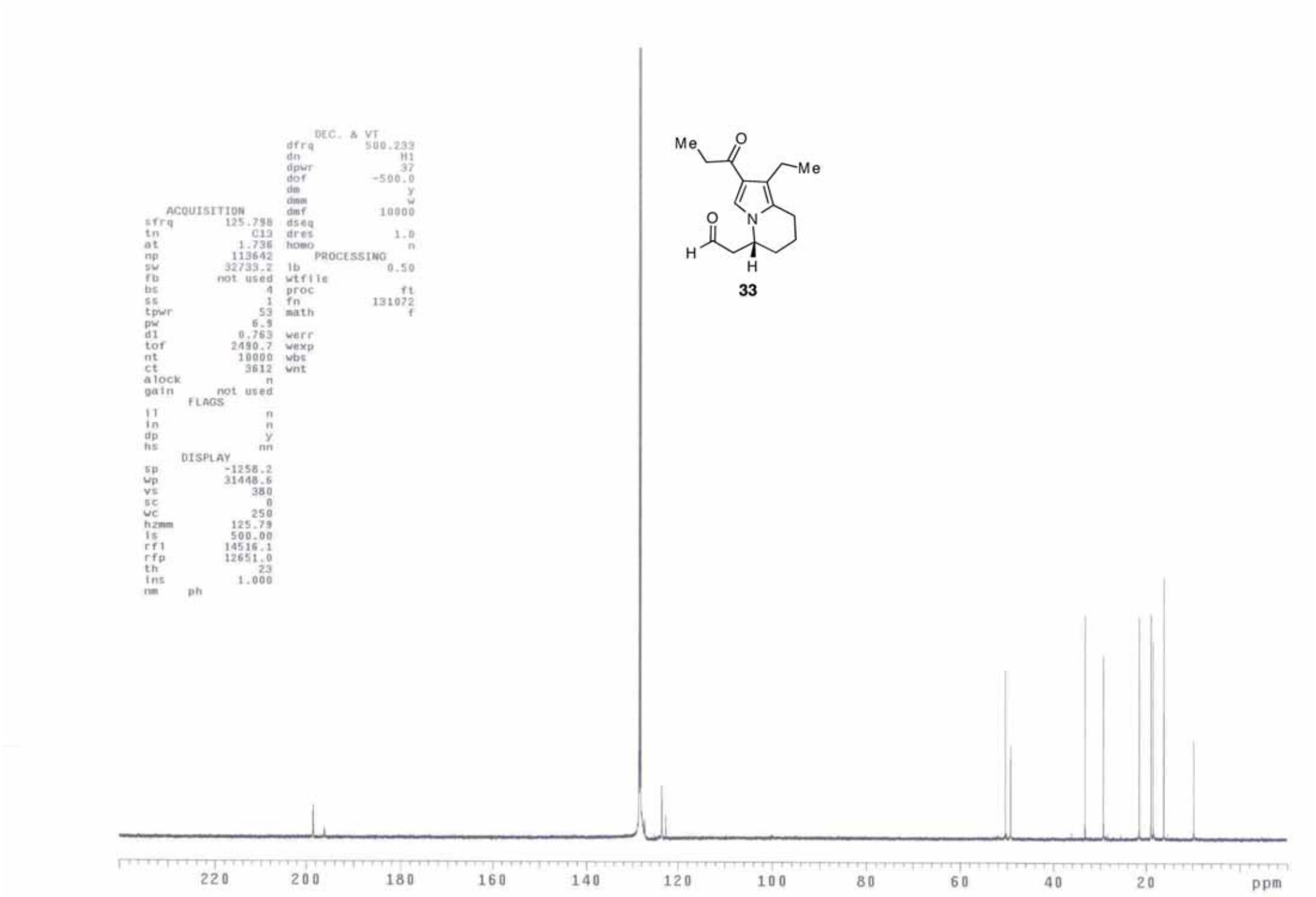


33

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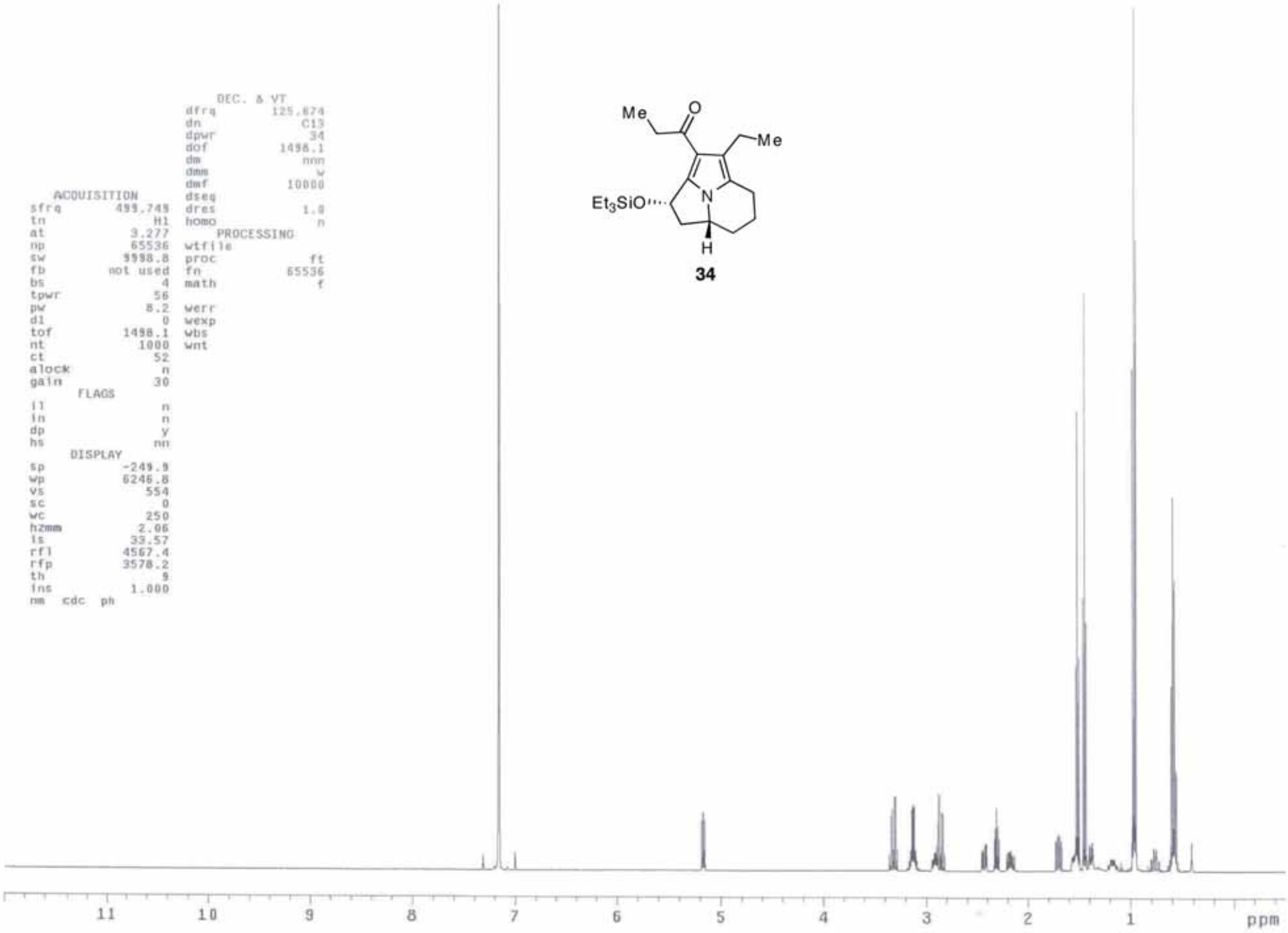
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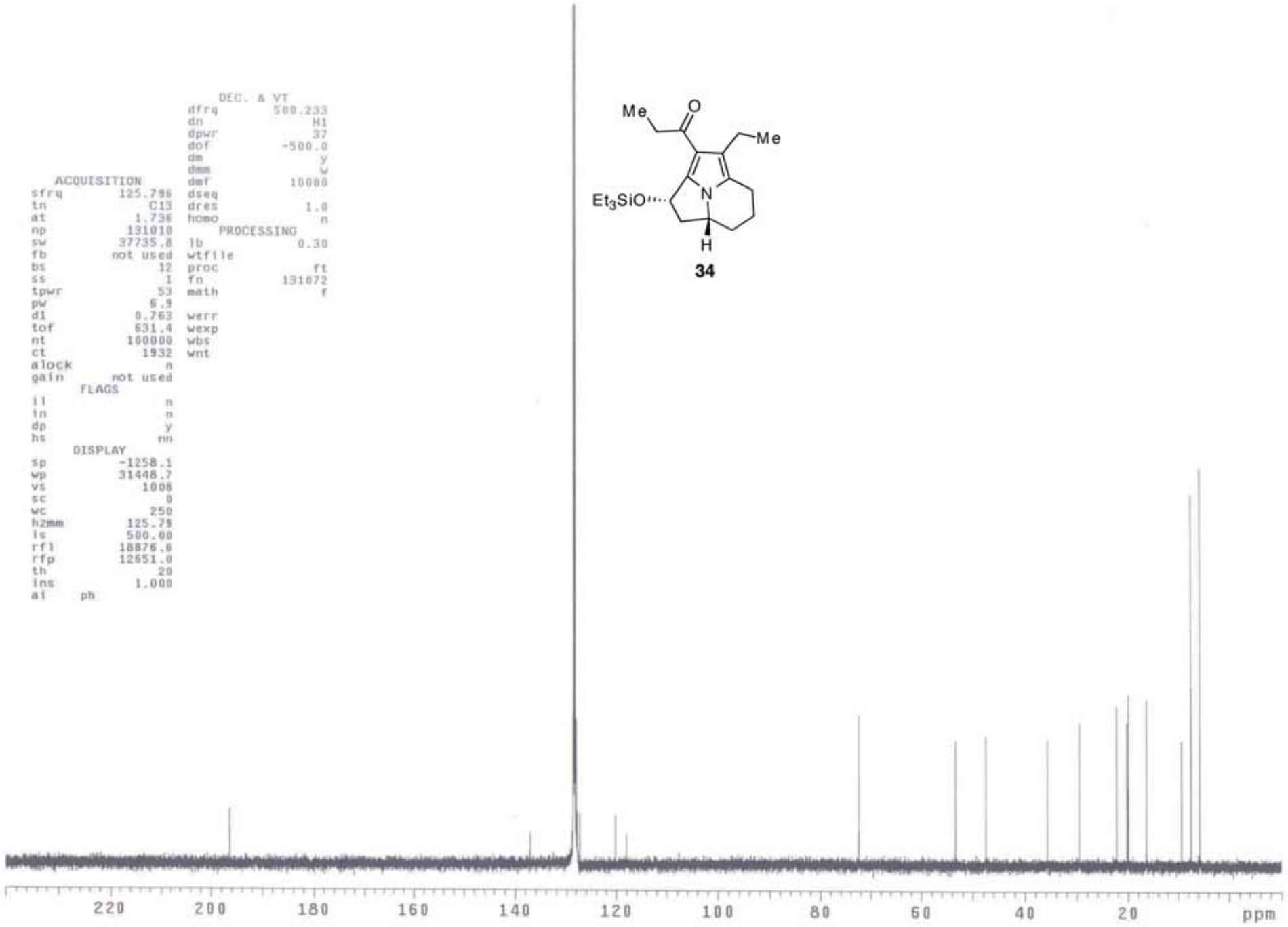
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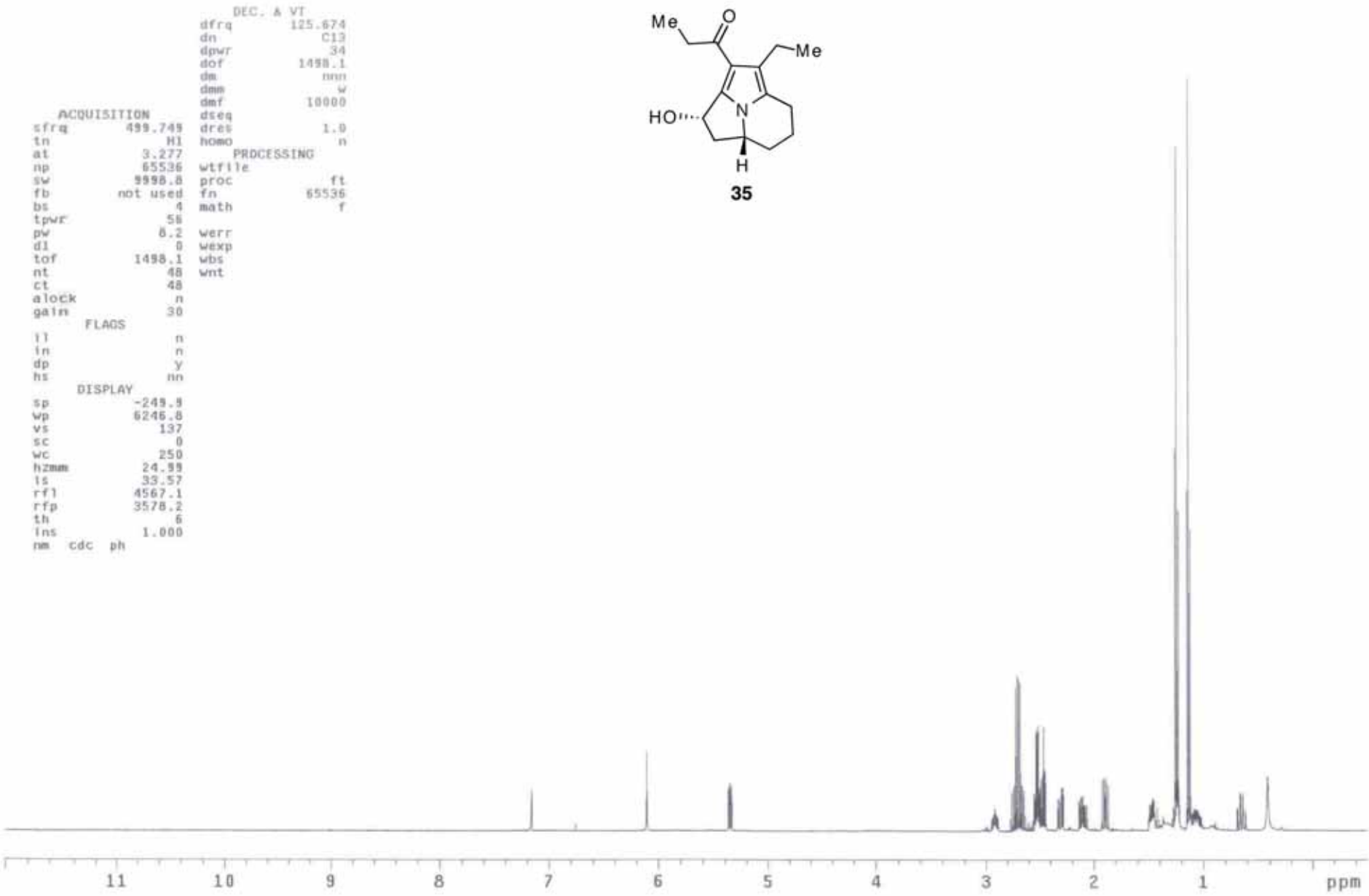
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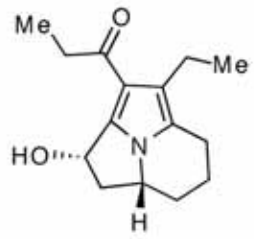

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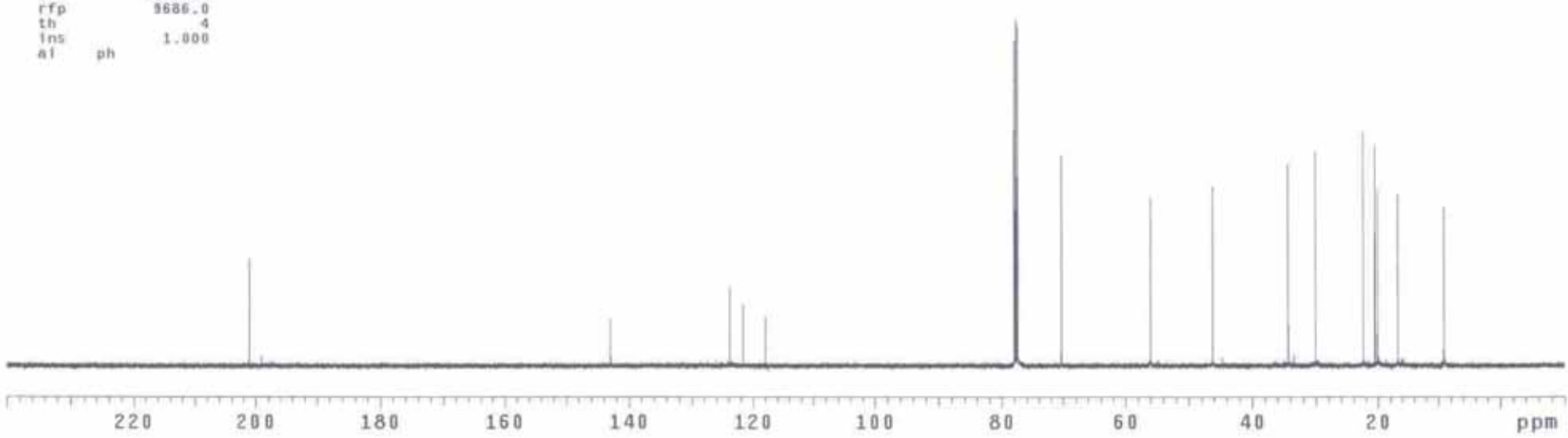

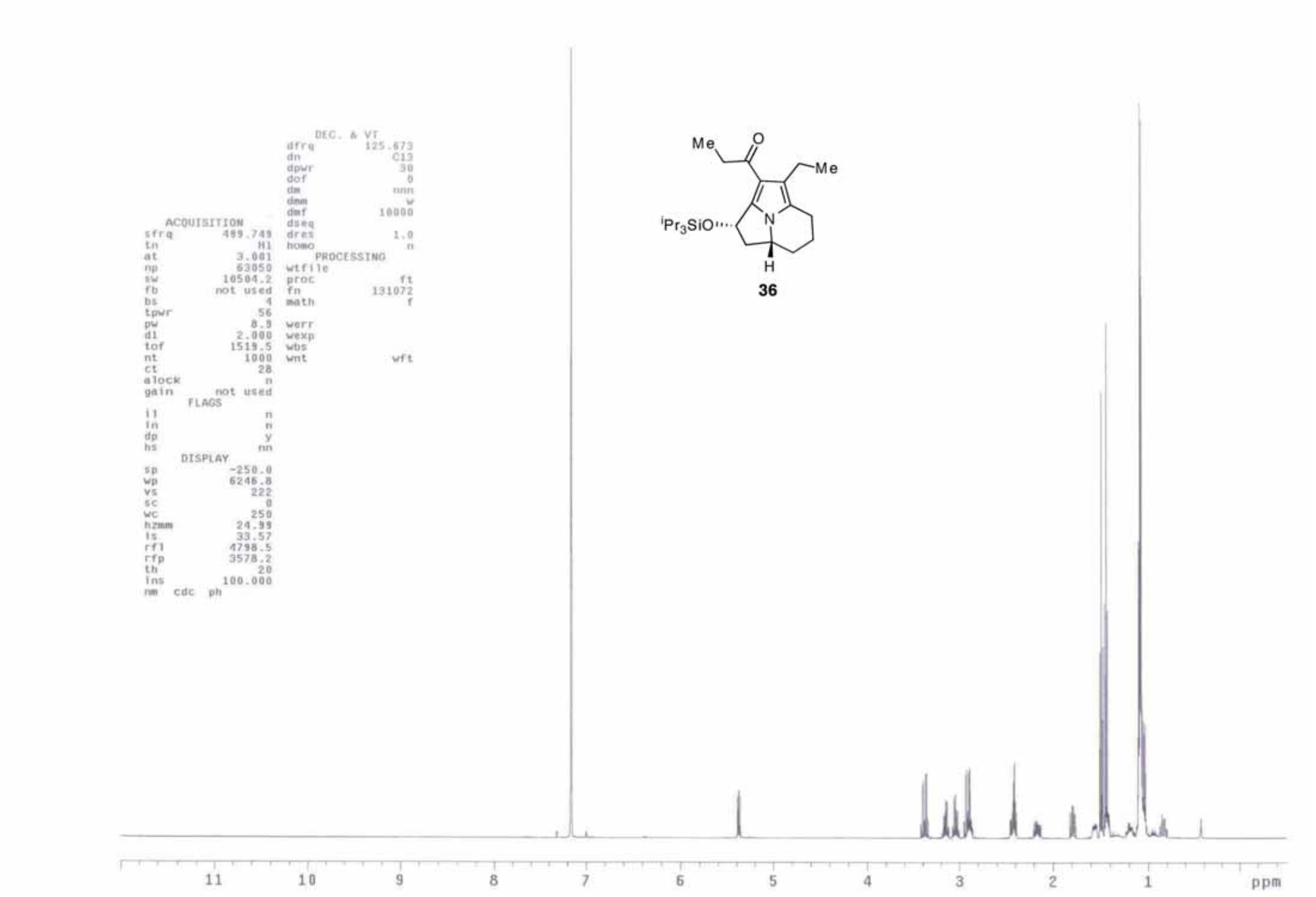
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werr
wexp
wbs
wnt wft
Me
O
Me
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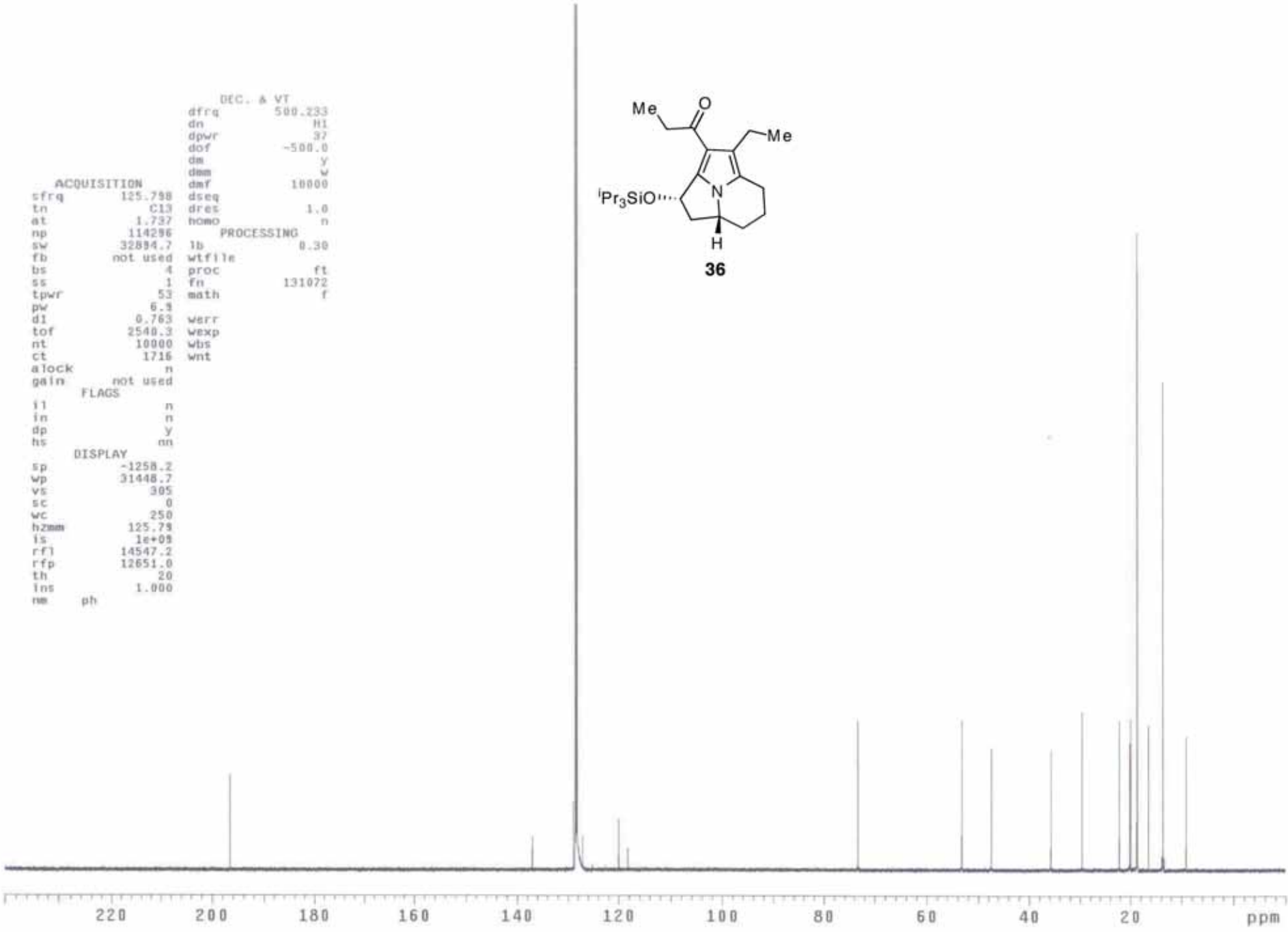
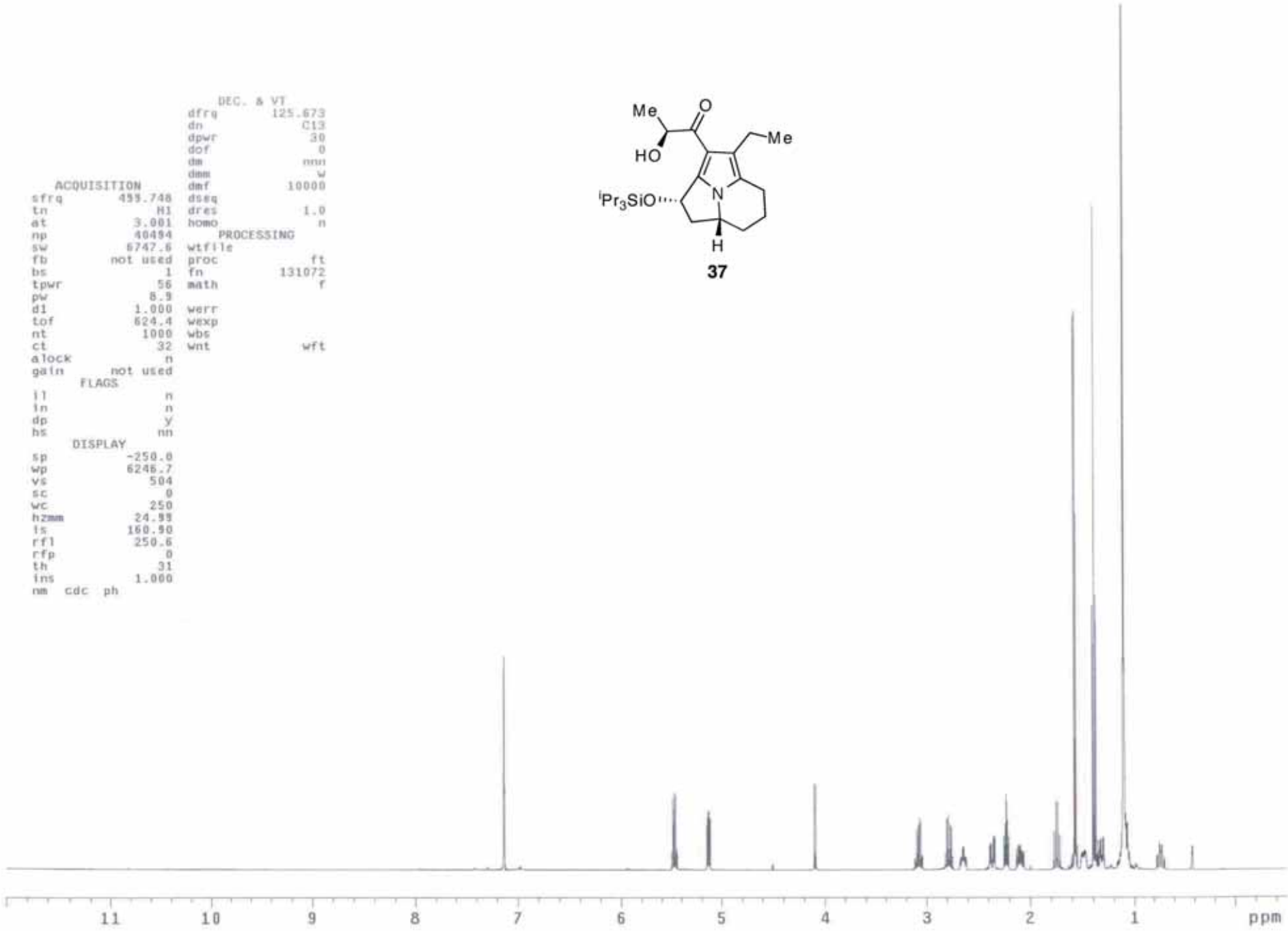
N
H
36
11
10
9
8
7
6
5
4
3
2
1
ppm

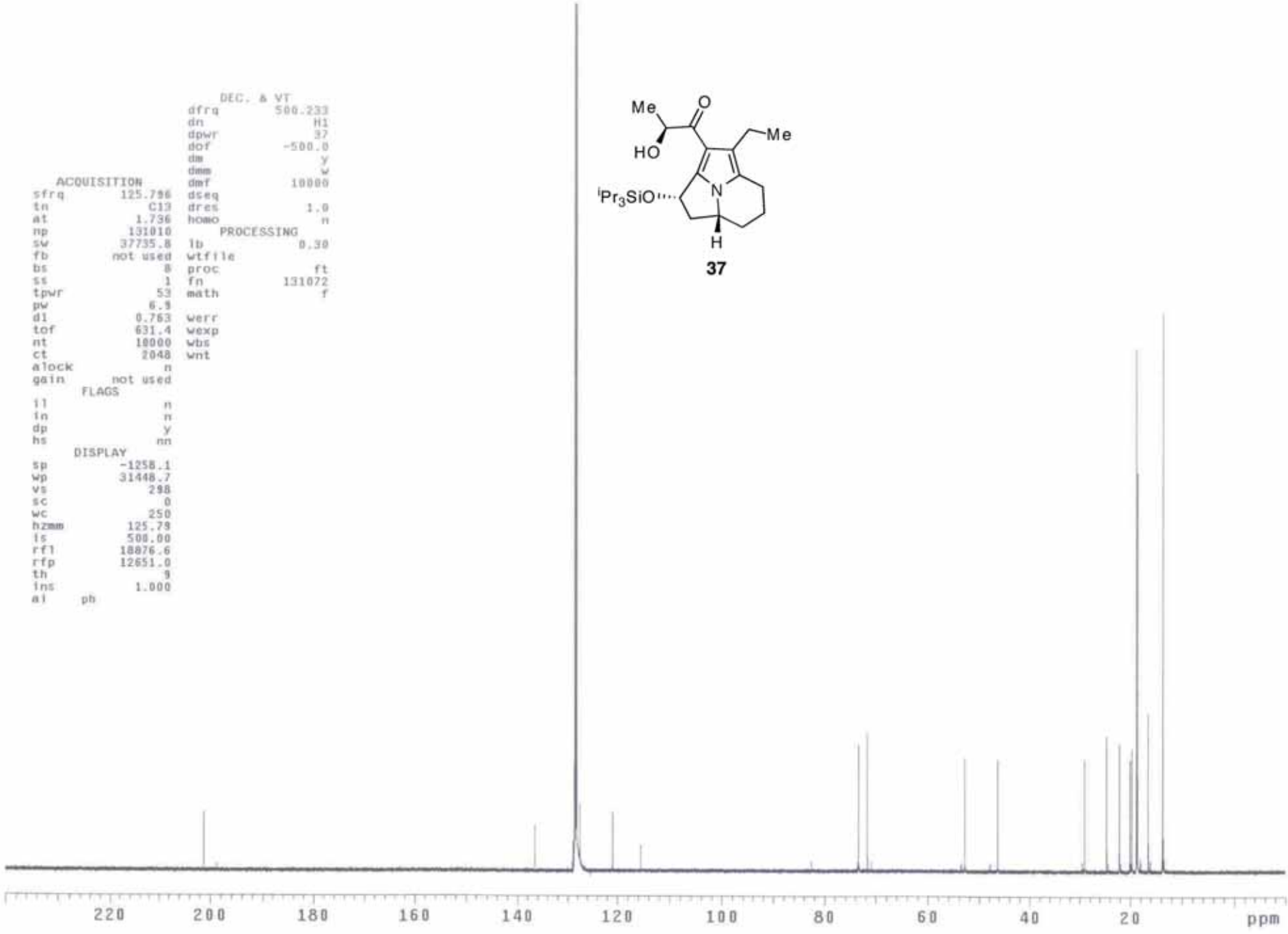

ACQUISITION
sfrq 125.798
tn C13
at 1.737
np 114296
sw 32894.7
fb not used
bs 4
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2540.3
nt 10000
ct 1716
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.2
wp 31448.7
vs 305
sc 0
wc 250
hzmm 125.79
is 1e+09
rfl 14547.2
rfp 12651.0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
Me
iPr3SiO
N
H
36
220
200
180
160
140
120
100
80
60
40
20
ppm

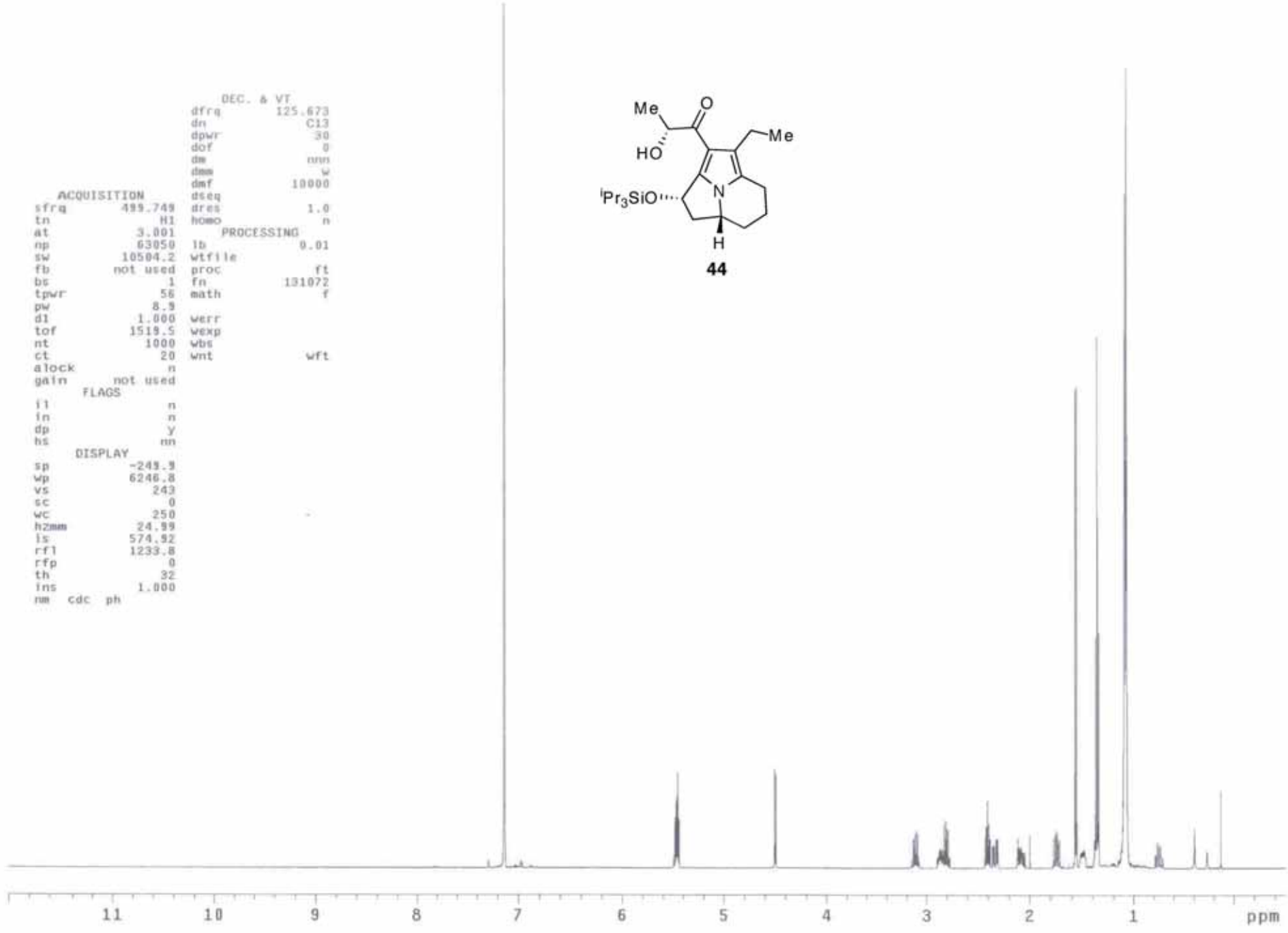
ACQUISITION
sfrq 499.748
tn H1
at 3.001
np 40494
sw 6747.6
fb not used
bs 1
tpwr 56
pw 8.9
d1 1.000
tof 624.4
nt 1000
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.7
vs 504
sc 0
wc 250
hzmm 24.99
is 160.90
rfl 250.6
rfp 0
th 31
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft

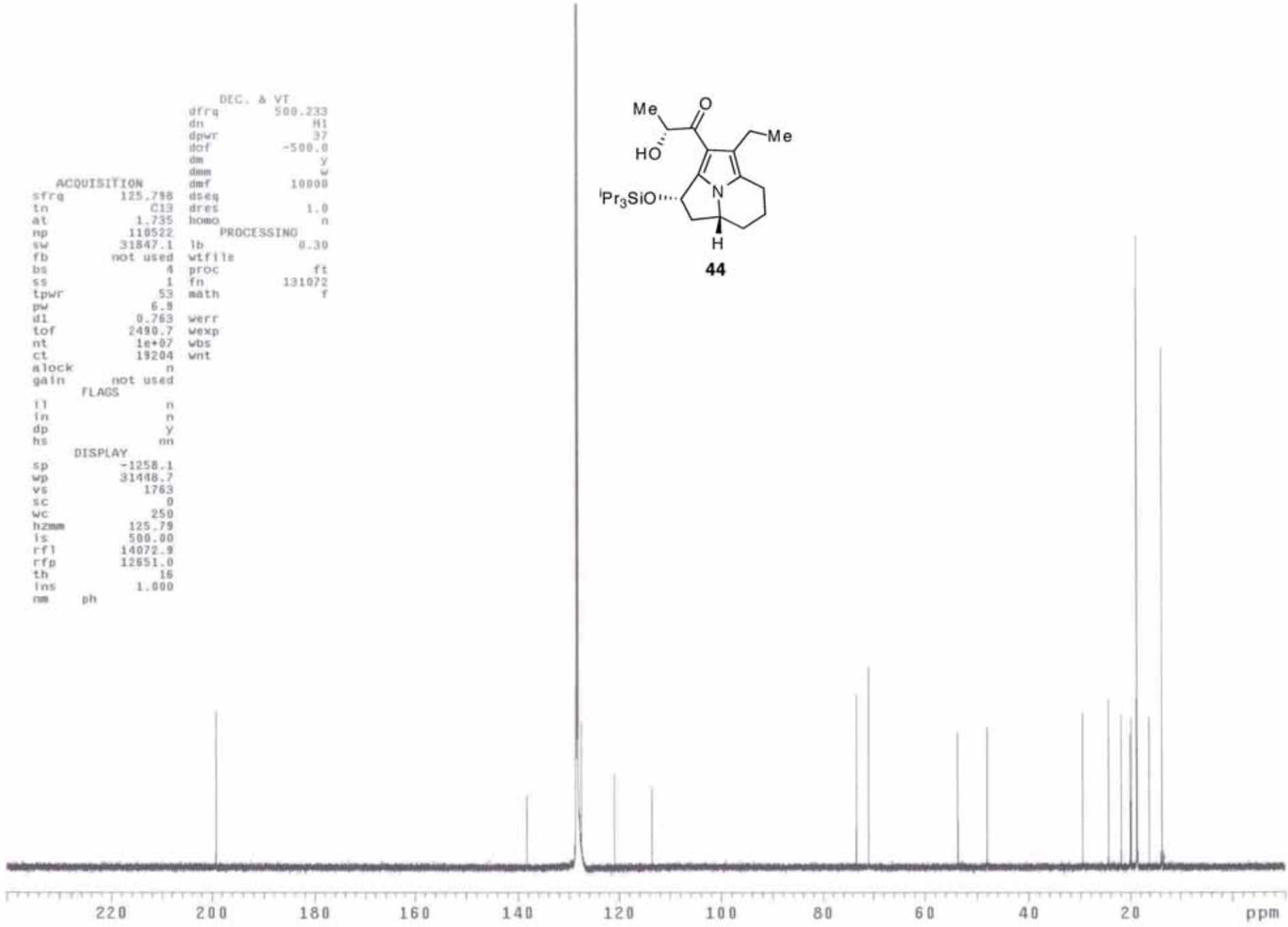
Me
O
HO
Me
$^{i}Pr_3SiO$
N
H

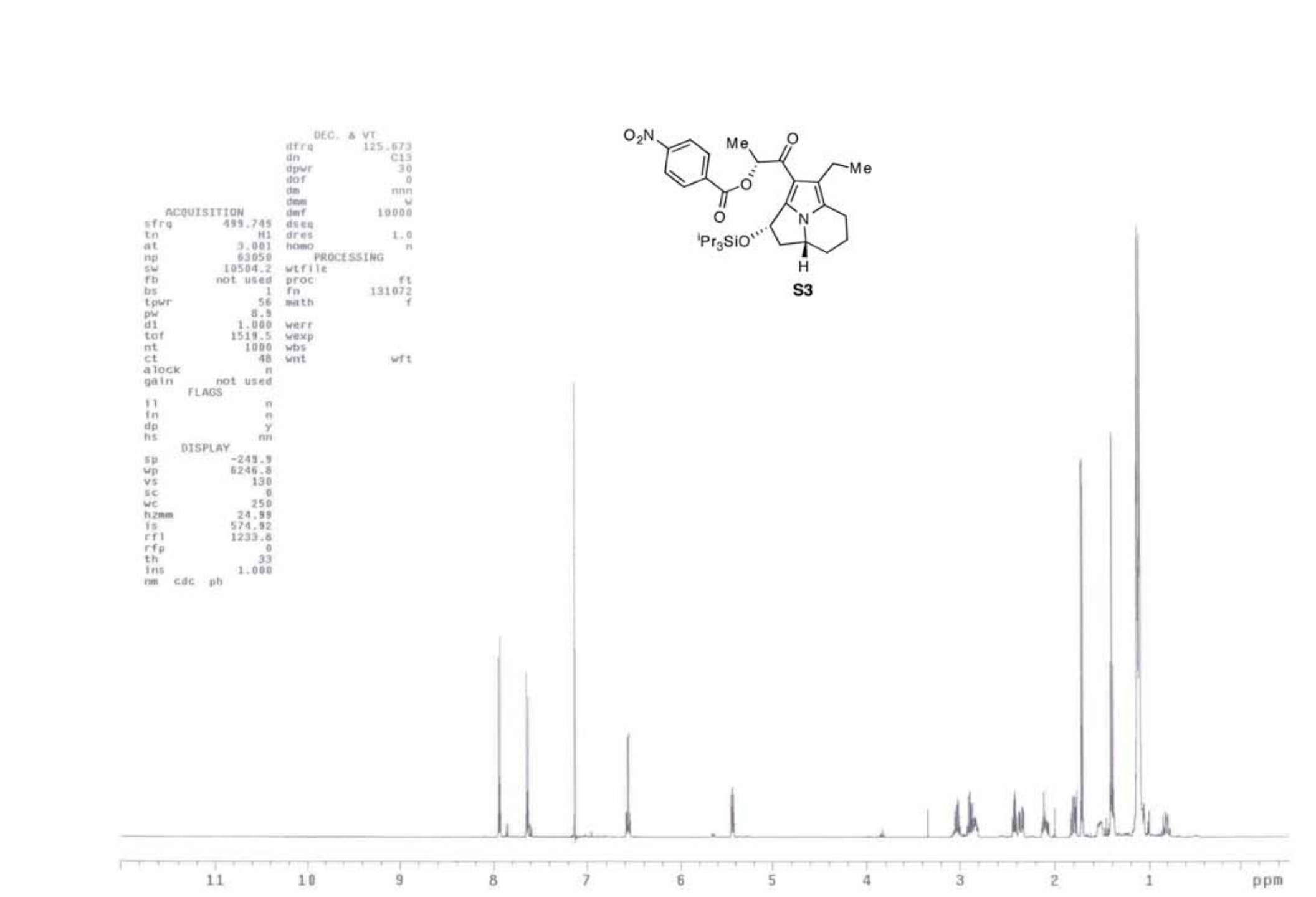
37

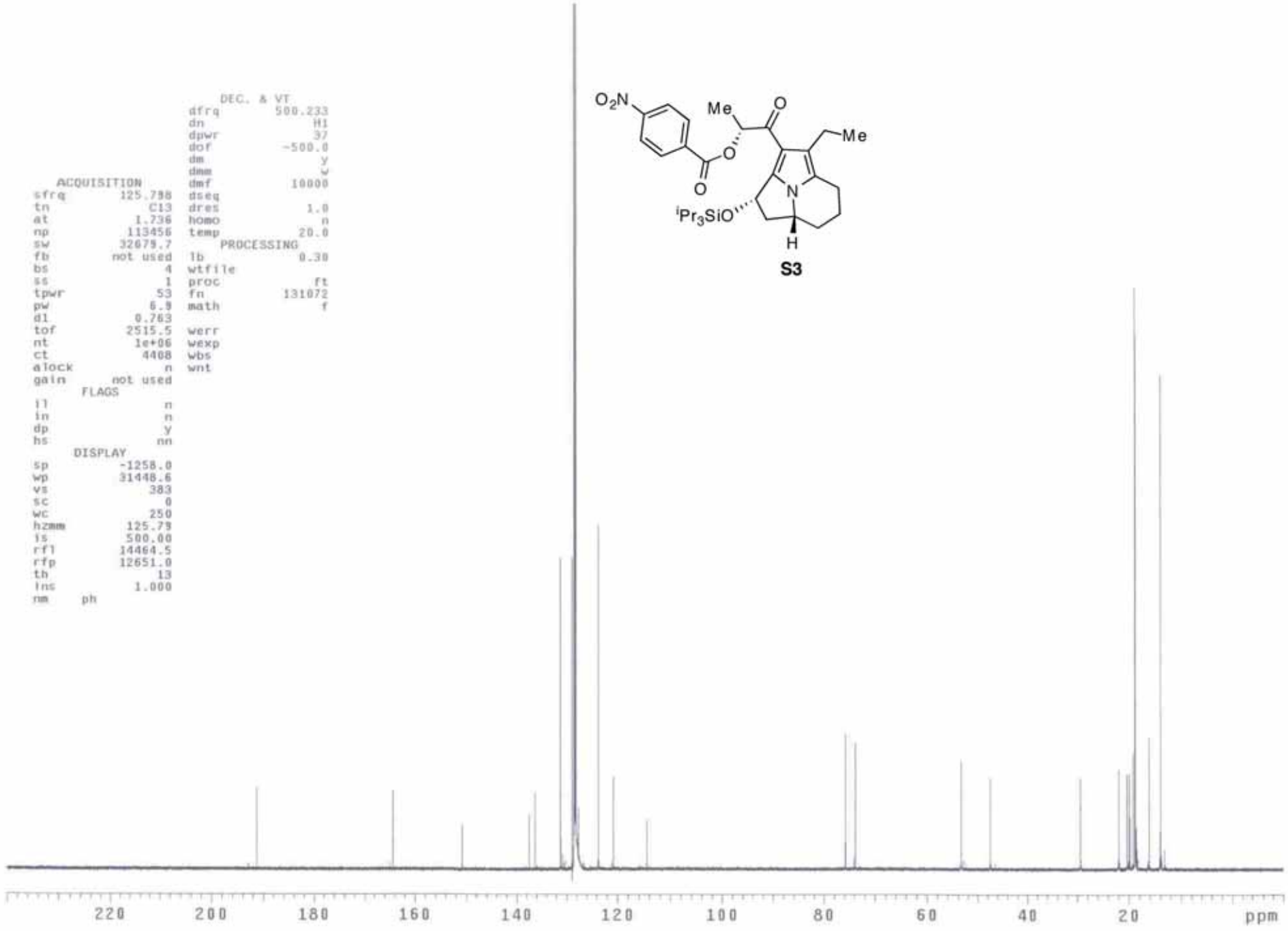

11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.786
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 10000
ct 2048
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.1
wp 31448.7
vs 298
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 18876.6
rfp 12651.0
th 9
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
HO
Me
iPr3SiO
N
H
37
220
200
180
160
140
120
100
80
60
40
20
ppm

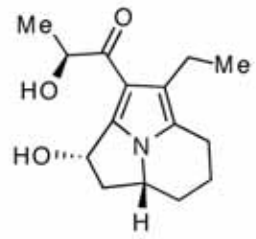

ACQUISITION
sfrq 499.749
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.9
d1 1.000
tof 1519.5
nt 1000
ct 20
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6246.8
vs 243
sc 0
wc 250
hzmm 24.99
is 574.92
rfl 1233.8
rfp 0
th 32
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.01
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft
Me
O
HO
Me
iPr3SiO
N
H
44
11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.798
tn C13
at 1.735
np 110522
sw 31847.1
fb not used
bs 4
ss 1
tpwr 53
pw 6.8
d1 0.763
tof 2490.7
nt 1e+07
ct 19204
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.1
wp 31448.7
vs 1763
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 14072.9
rfp 12651.0
th 16
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
HO
Me
iPr3SiO
N
H
44
220
200
180
160
140
120
100
80
60
40
20
ppm

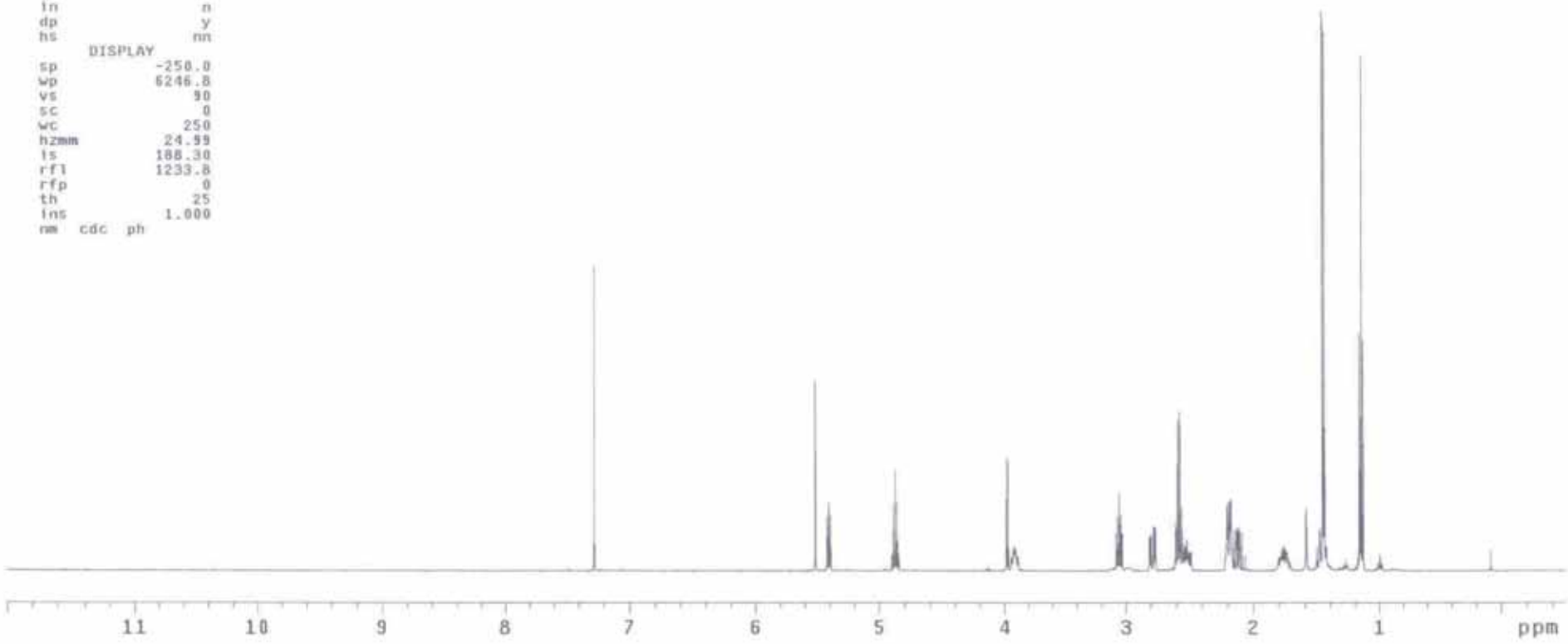

ACQUISITION
sfrq 499.749
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.9
d1 1.000
tof 1519.5
nt 1000
ct 48
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6246.8
vs 130
sc 0
wc 250
hzmm 24.99
is 574.92
rfl 1233.8
rfp 0
th 33
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft
O2N
Me
O
Me
O
O
N
iPr3SiO
H
S3
11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.788
tn C13
at 1.736
np 113456
sw 32679.7
fb not used
bs 4
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2515.5
nt 1e+06
ct 4408
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.0
wp 31448.6
vs 383
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 14464.5
rfp 12651.0
th 13
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
O2N
Me
O
O
O
Me
N
iPr3SiO
H
S3
220
200
180
160
140
120
100
80
60
40
20
ppm

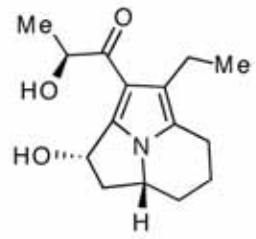
ACQUISITION		DEC. & VT	
sfrq	499.749	frq	125.673
tn	H1	n	C13
at	3.001	pwr	30
np	63050	of	0
sw	10504.2	m	nnn
fb	not used	mm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.9	dres	1.0
d1	1.000	homo	n
tof	1519.5	PROCESSING	
nt	100	lb	0.00
ct	12	wtfile	
alock	n	proc	ft
gain	not used	fn	131072
FLAGS		math	f
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	wft
DISPLAY			
sp	-250.0		
wp	6246.8		
vs	90		
sc	0		
wc	250		
hzmm	24.99		
is	188.30		
rfl	1233.8		
rfp	0		
th	25		
ins	1.000		
nm cdc ph			



38



ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	1.736	dpwr	37
np	131010	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	4	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	631.4	lb	0.30
nt	1e+07	wtfile	
ct	1168	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
sp	-1258.3		
wp	31448.1		
vs	65		
sc	0		
wc	250		
hzmm	125.79		
is	500.00		
rfl	15911.8		
rfp	9686.0		
th	6		
ins	1.000		
nm	ph		



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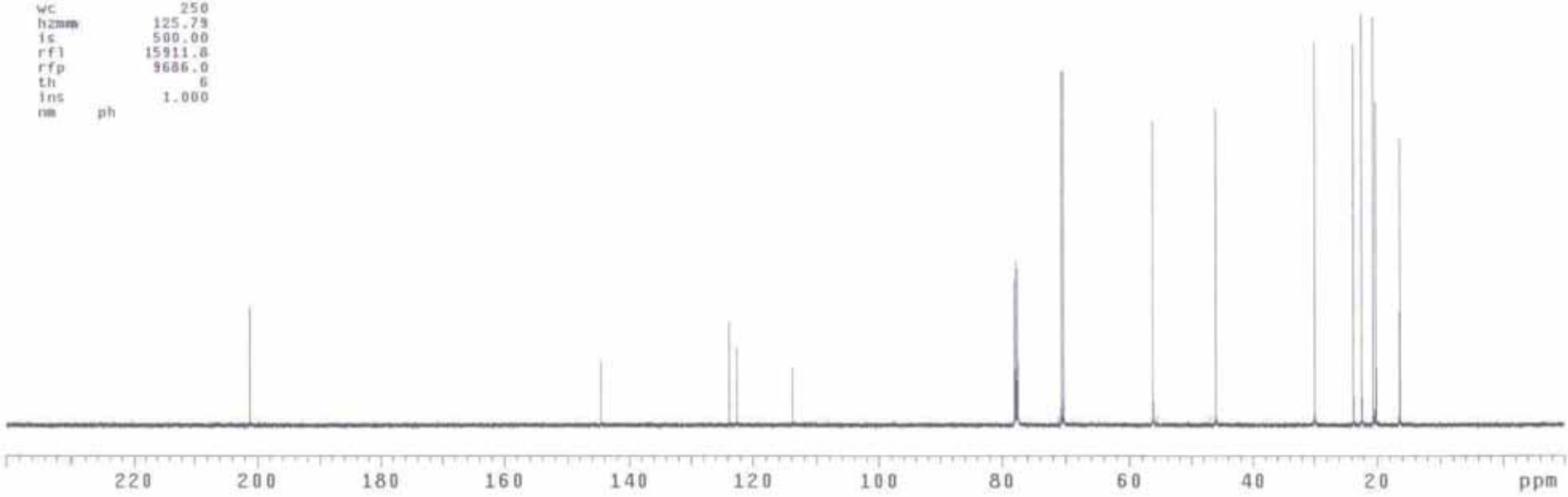


ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	40484
sw	6747.6
fb	not used
bs	1
tpwr	56
pw	8.5
d1	1.000
tof	624.4
nt	1000
ct	24
alock	n
gain	not used

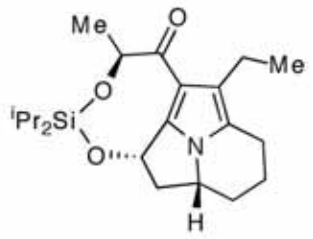
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-208.6
wp	6242.1
vs	90
sc	0
wc	250
hzmm	24.97
is	321.72
rfl	208.7
rfp	0
th	25
ins	1.000

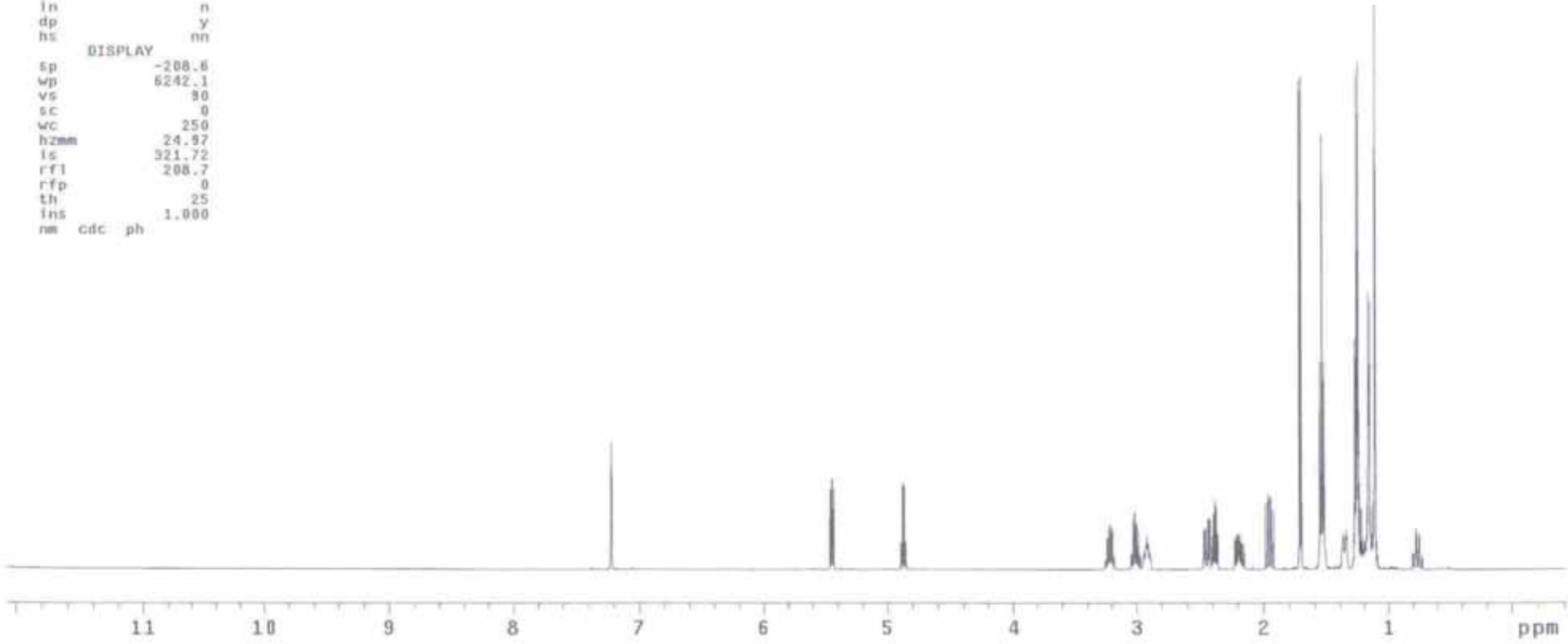
nm cdc ph

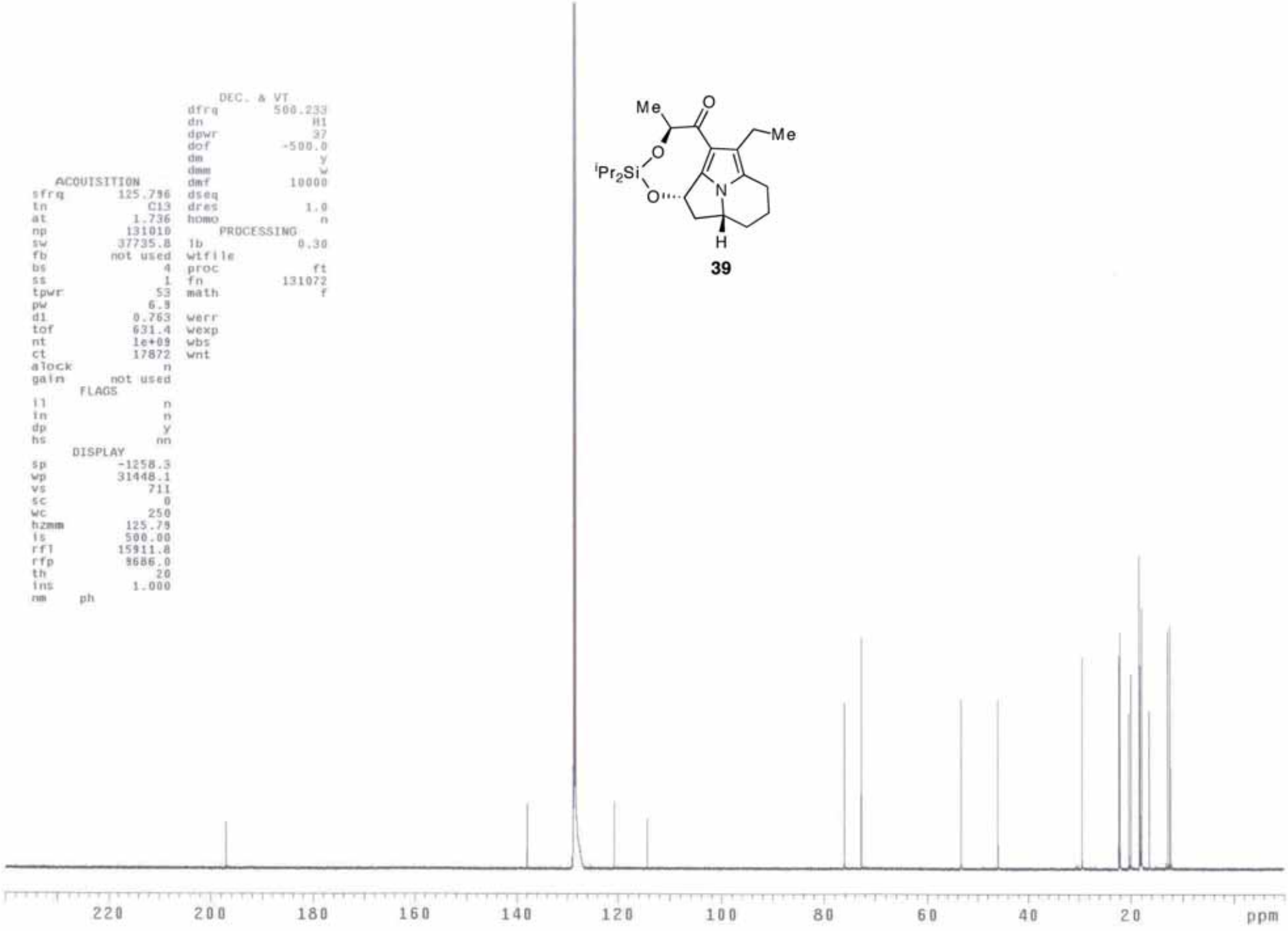
DEC. & VT	
dfrq	125.673
dn	C13
dpwr	38
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

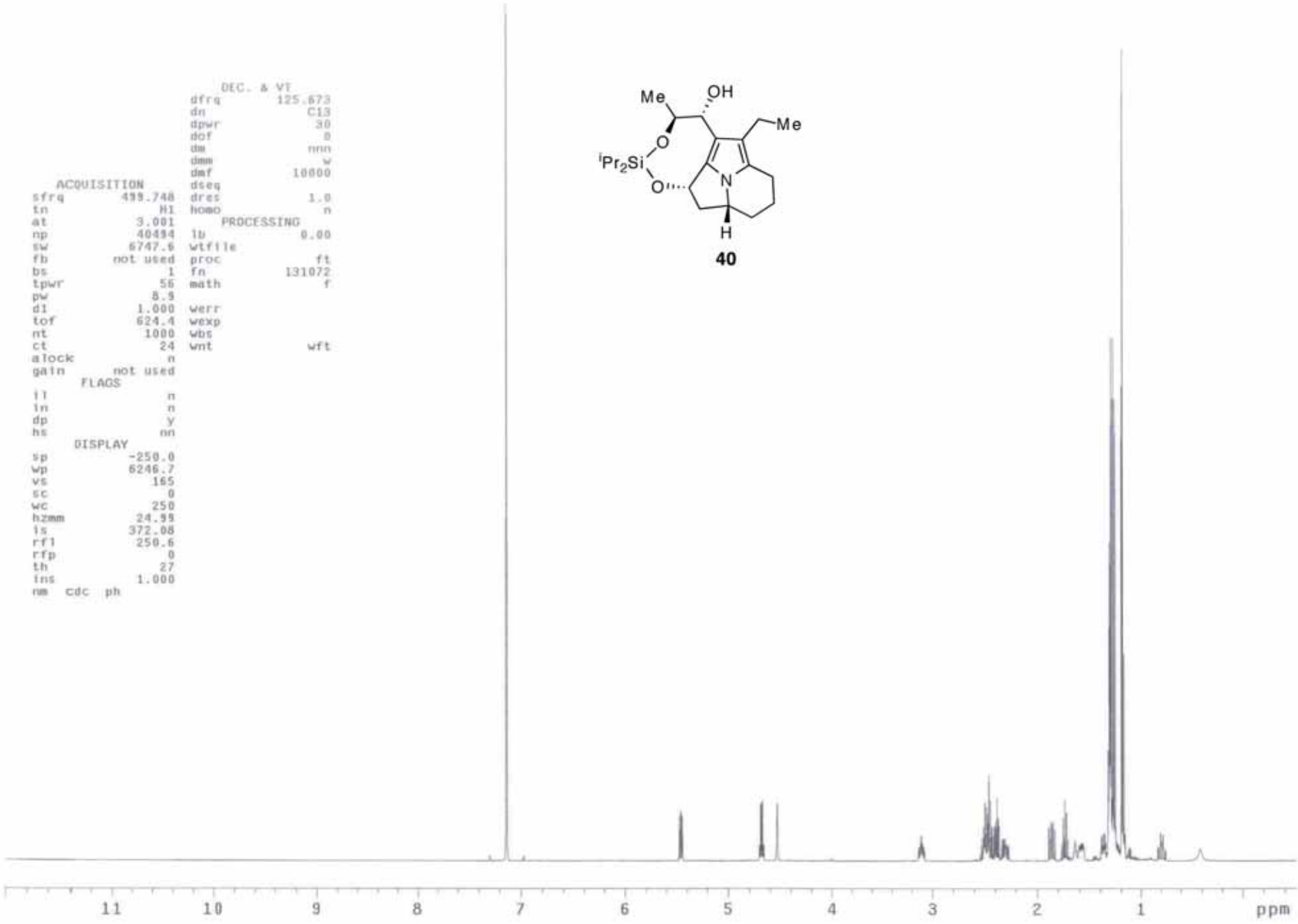
PROCESSING	
lb	0.05
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	wft

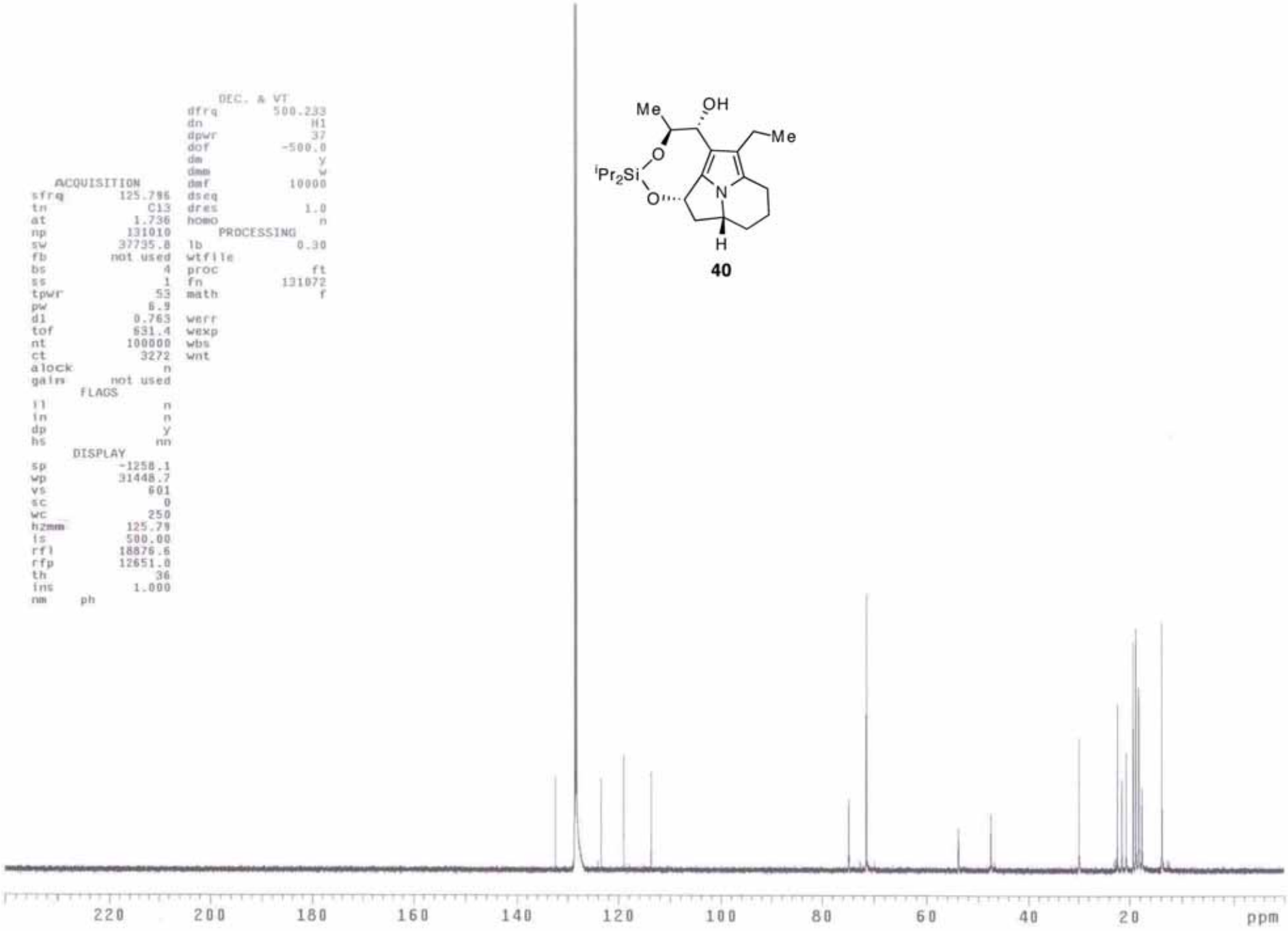


39




ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 4
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+09
ct 17872
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.1
vs 711
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 15911.8
rfp 9686.0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
Me
$^{i}Pr_2Si$
O
O
N
H
39
220
200
180
160
140
120
100
80
60
40
20
ppm


ACQUISITION
sfrq 499.748
tn H1
at 3.001
np 40494
sw 6747.6
fb not used
bs 1
tpwr 56
pw 8.9
d1 1.000
tof 624.4
nt 1000
ct 24
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.7
vs 165
sc 0
wc 250
hzmm 24.99
is 372.08
rf1 250.6
rfp 0
th 27
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft
Me
OH
Me
iPr2Si
O
O
N
H
40
11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.786
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 4
ss 1
tpwr 53
pw 8.9
d1 0.763
tof 631.4
nt 100000
ct 3272
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.1
wp 31448.7
vs 601
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 18876.6
rfp 12651.0
th 36
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
OH
Me
$^{i}Pr_2Si$
O
O
N
H
40
220
200
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION	
sfrq	499.748
tn	H1
at	3.001
np	40494
sw	6747.6
fb	not used
bs	1
tpwr	56
pw	8.9
d1	1.000
tof	624.4
nt	1000
ct	80
alock	n
gain	not used

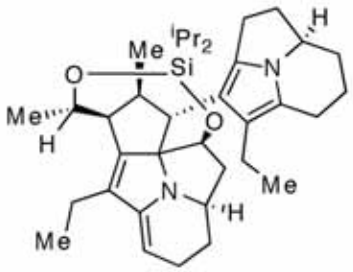
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-208.6
wp	6246.7
vs	135
sc	0
wc	250
hzmm	1.70
is	15.99
rfl	208.7
rfp	0
th	39
ins	3.000

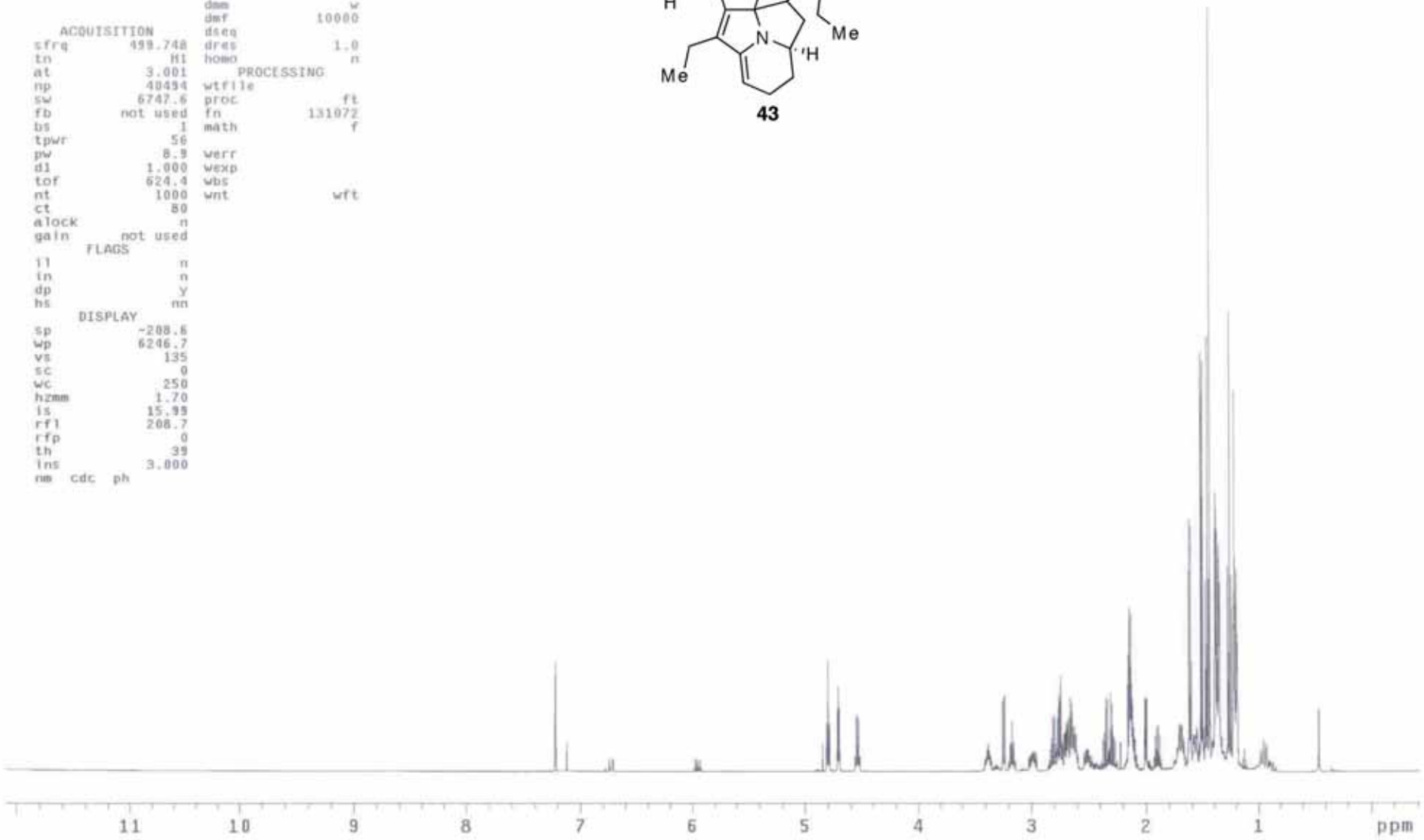
nm cdc ph

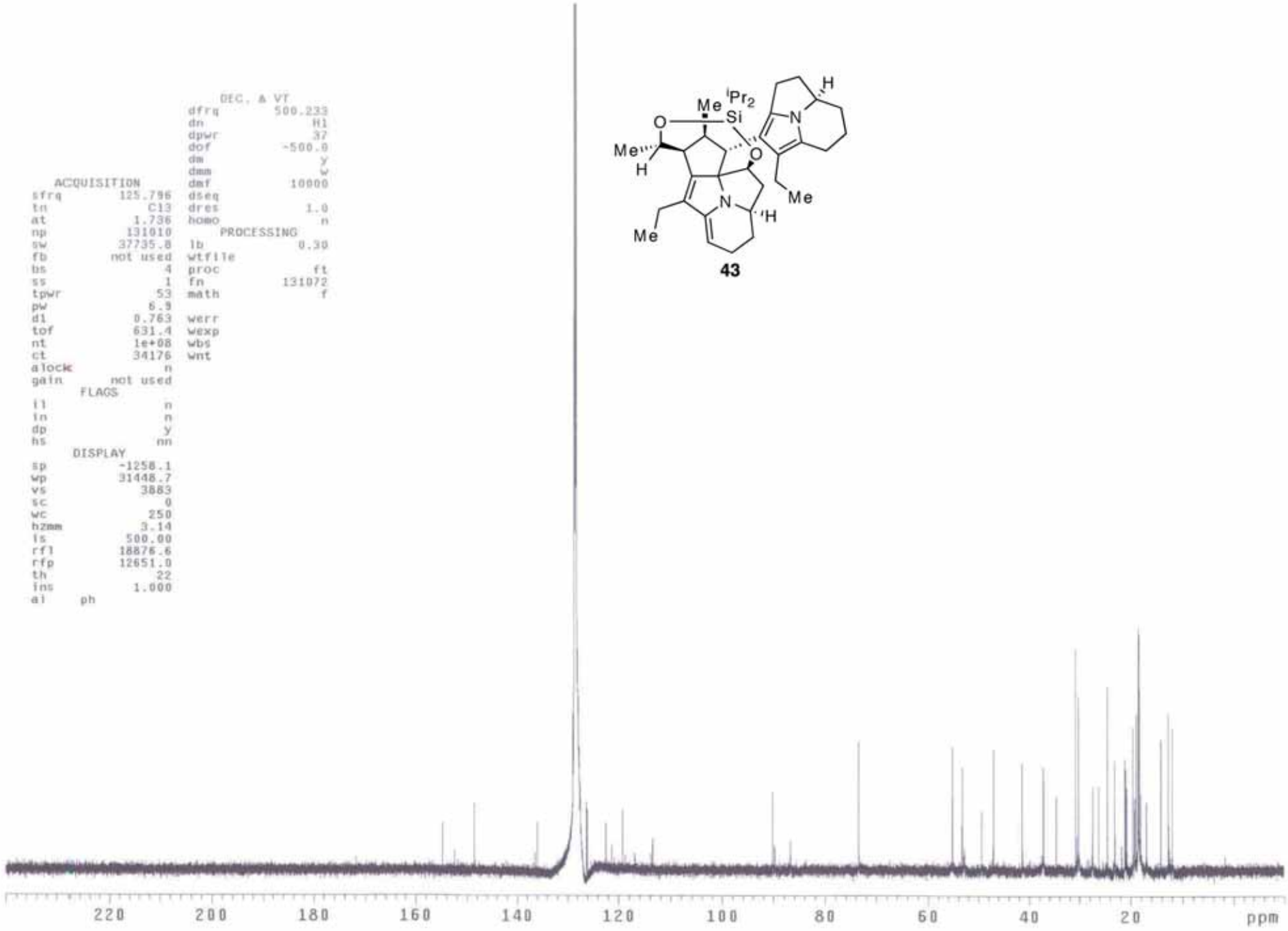
DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	wft

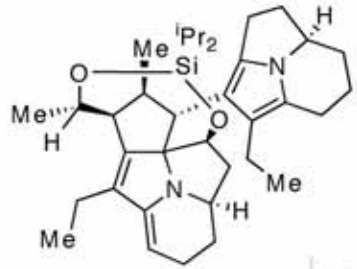


43




ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 4
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+08
ct 34176
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.1
wp 31448.7
vs 3883
sc 0
wc 250
hzmm 3.14
is 500.00
rfl 18876.6
rfp 12651.0
th 22
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
iPr2
Si
O
O
N
N
H
H
Me
Me
Me
H
43
220
200
180
160
140
120
100
80
60
40
20
ppm

Relax. delay 1.000 sec
Acq. time 0.269 sec
Width 3807.3 Hz
2D Width 3807.3 Hz
Single scan
256 increments
OBSERVE H1, 499.7446560 MHz
DATA PROCESSING
Sq. sine bell 0.134 sec
F1 DATA PROCESSING
Sq. sine bell 0.067 sec
FT size 2048 x 2048
Total time 0 min, -1 sec



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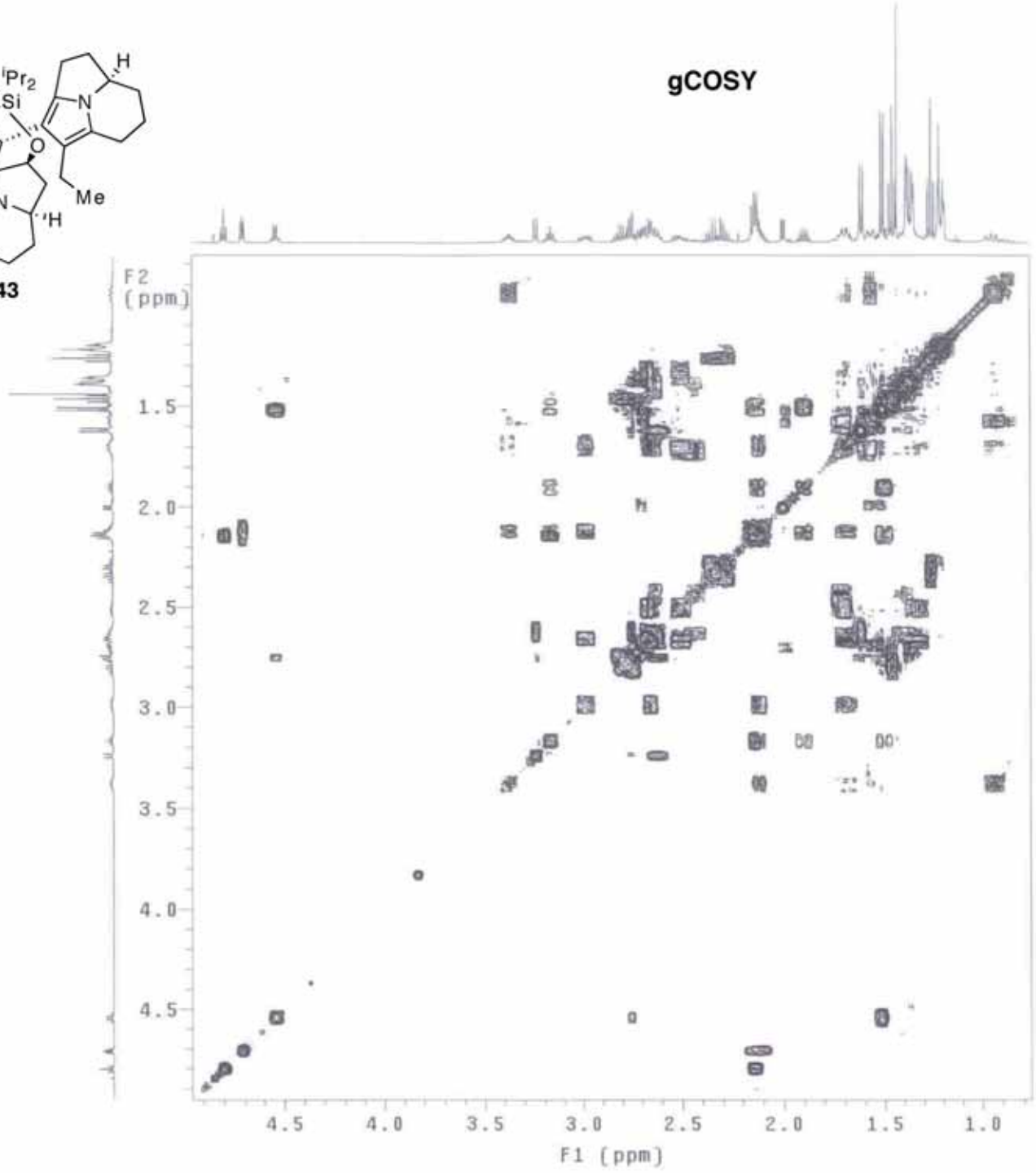
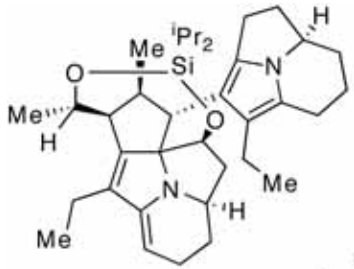
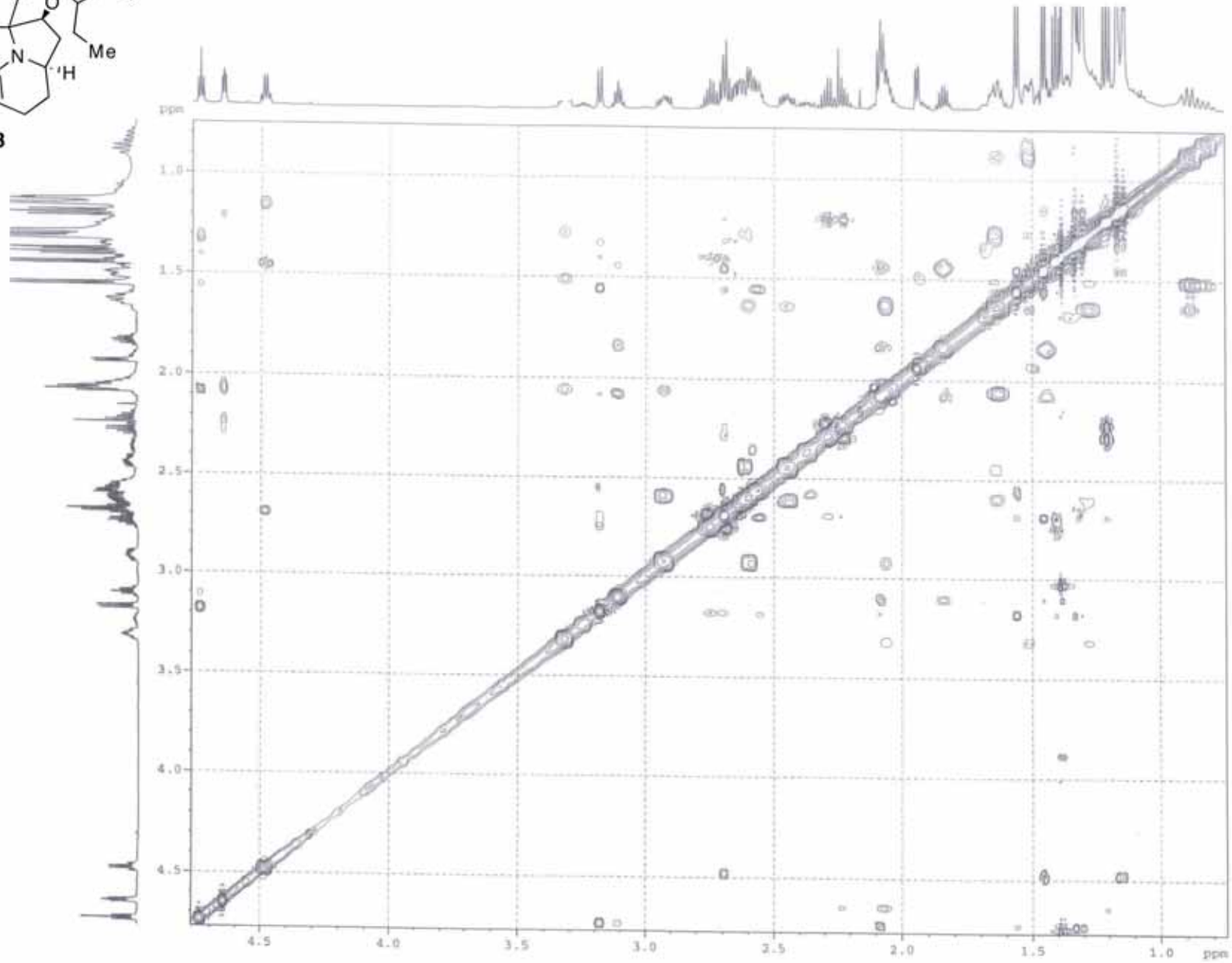
gCOSY



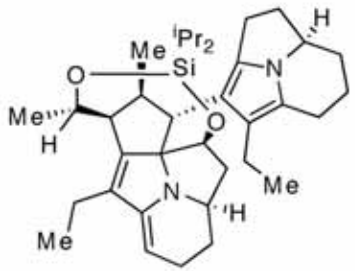

Me
iPr2
Si
O
O
Me
H
N
H
N
H
Me
Me

43

NOESY


ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

HSQC



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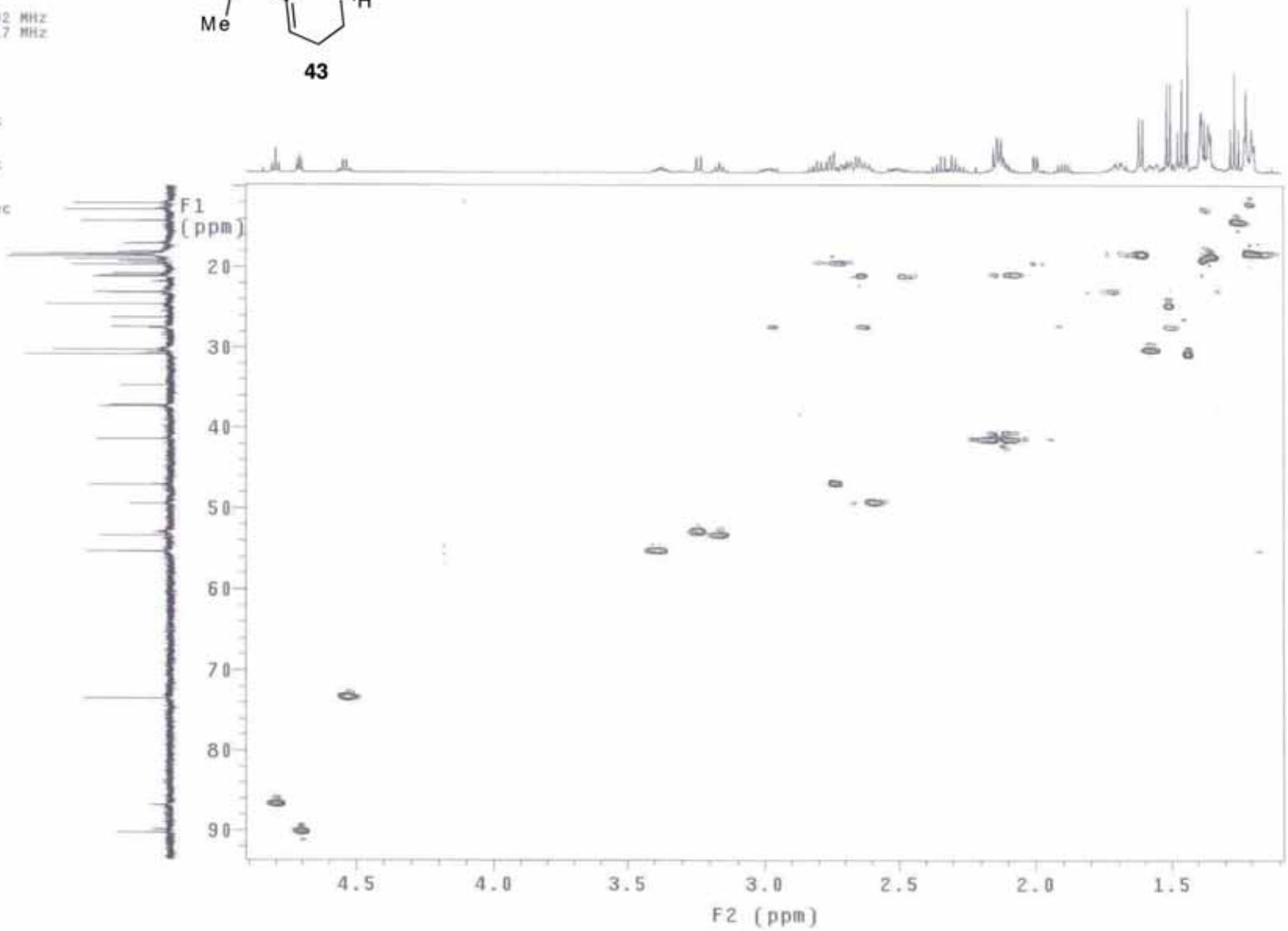
```
PULSE SEQUENCE: HSQC
 Relax. delay 1.000 sec
 Acq. time 0.100 sec
 Width    3807.3 Hz
 2D Width 25931.9 Hz
 2 repetitions
 2 x 200 increments
OBSERVE   H1, 499.7446592 MHz
DECOUPLE C13, 125.6731217 MHz
 Power 52 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Sq. sine bell 0.100 sec
  Shifted by -0.100 sec
F1 DATA PROCESSING
 Sq. sine bell 0.020 sec
  Shifted by -0.020 sec
FT size 1024 x 2048
Total time 16 min, 22 sec
```



ACQUISITION	
sfrq	499.749
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	1
tpwr	56
pw	8.5
d1	1.000
tof	1519.5
nt	1000
ct	24
alock	n
gain	not used

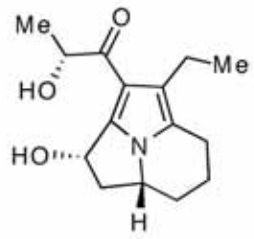
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-250.0
wp	6246.8
vs	107
sc	0
wc	250
hzmm	24.99
is	33.57
rfl	1233.8
rfp	0
th	7
ins	1.000

nm cdc ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
lb	0.01
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	wft



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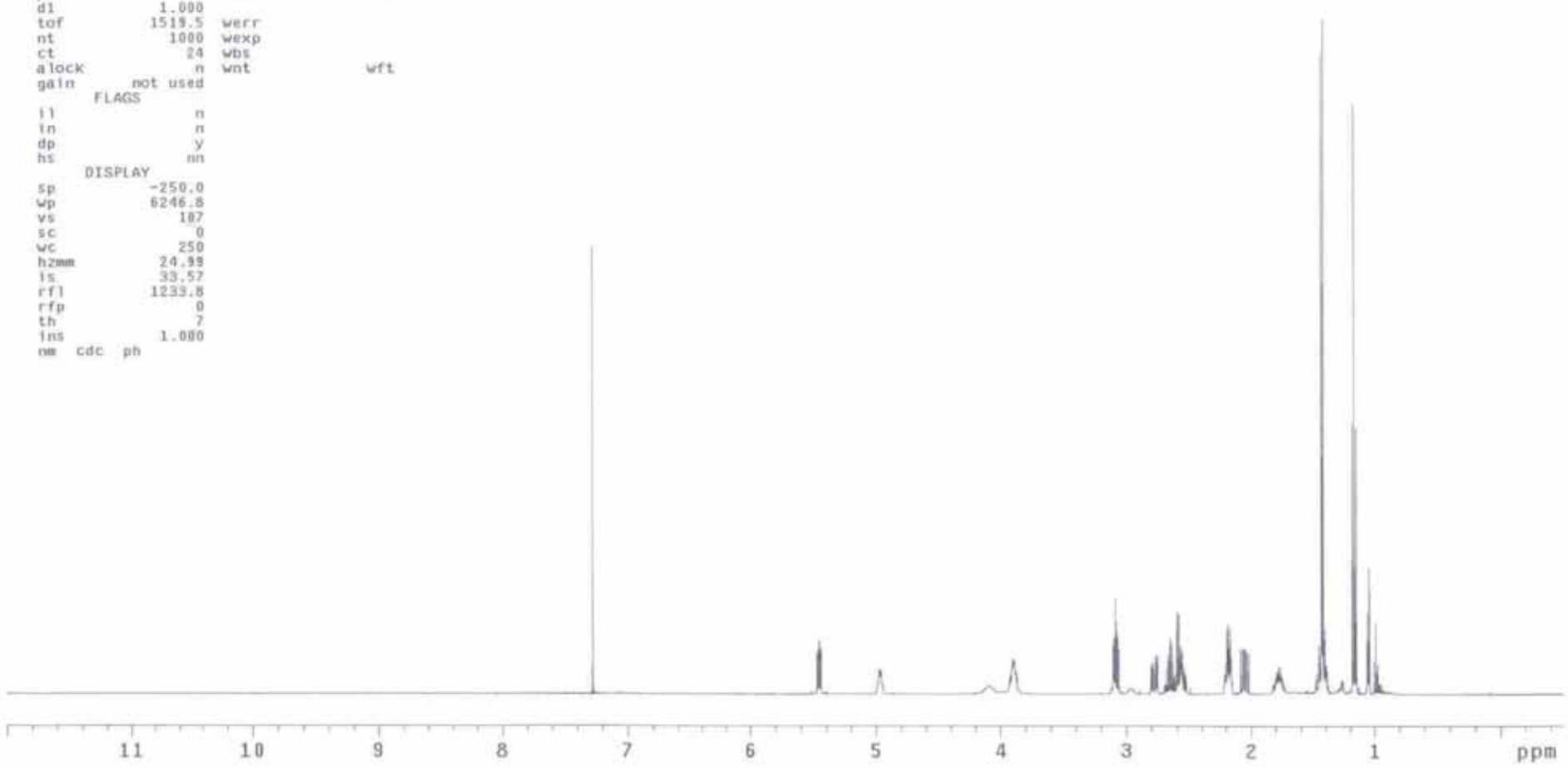
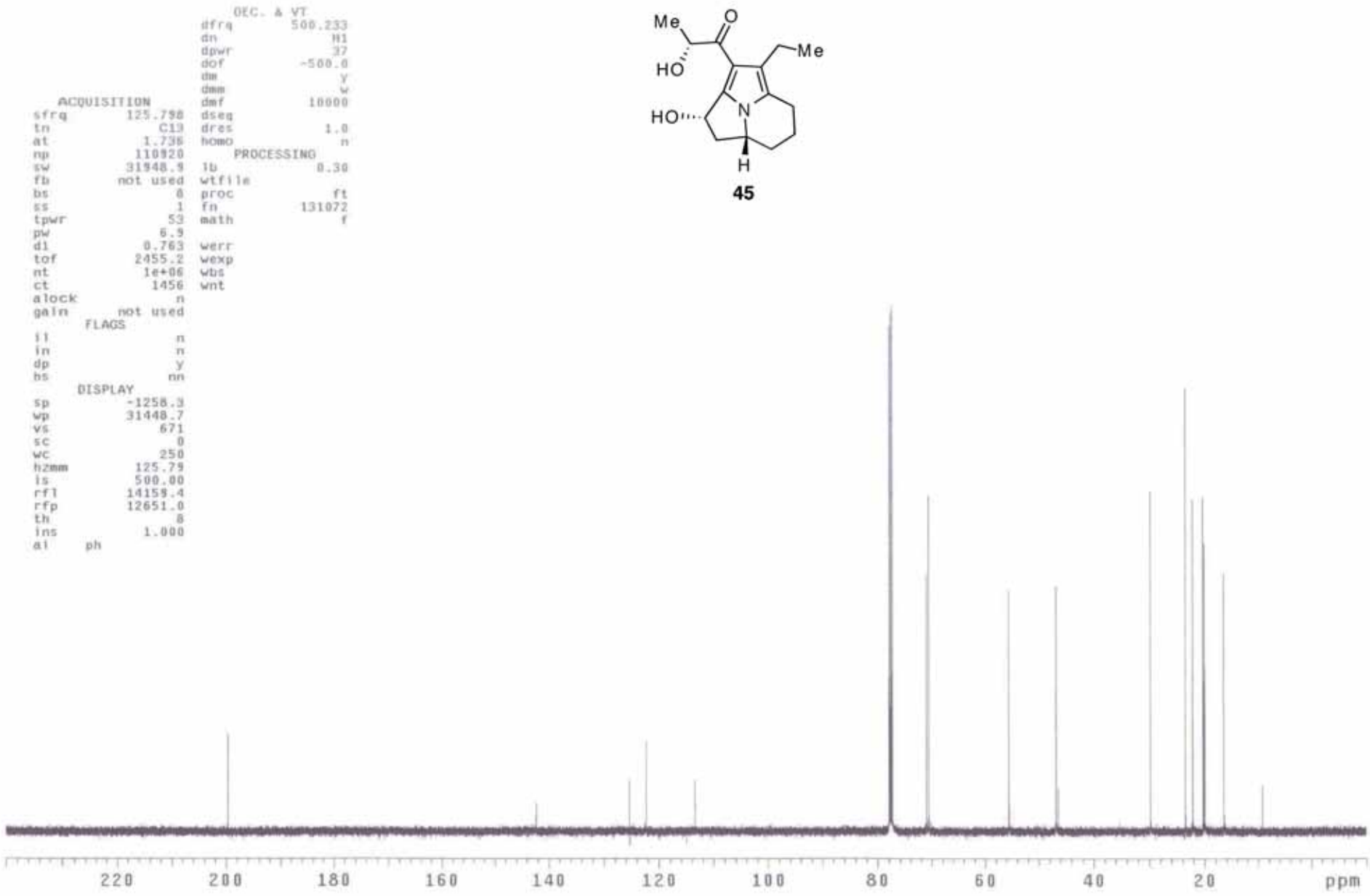



ACQUISITION
sfrq 125.798
tn C13
at 1.738
np 110920
sw 31948.9
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2455.2
nt 1e+06
ct 1456
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.7
vs 671
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 14159.4
rfp 12651.0
th 8
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
HO
Me
HO
N
H
45
220
200
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION	
sfrq	500.235
tn	H1
at	3.200
np	64000
sw	10000.0
fb	not used
bs	1
ss	1
tpwr	59
pw	9.8
d1	1.000
tof	1498.2
nt	10
ct	10
alock	n
gain	not used

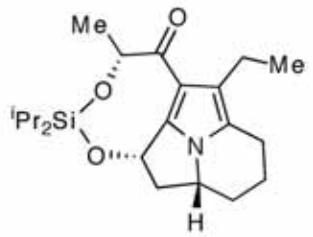
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-250.2
wp	6252.9
vs	87
sc	0
wc	250
hzmm	25.01
is	100.00
rf1	4577.3
rfp	3576.7
th	7
ins	1.000

nm cdc ph

DEC. & VT	
dfrq	125.785
dn	C13
dpwr	37
dof	0
dm	nnn
dmm	c
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
lb	0.00
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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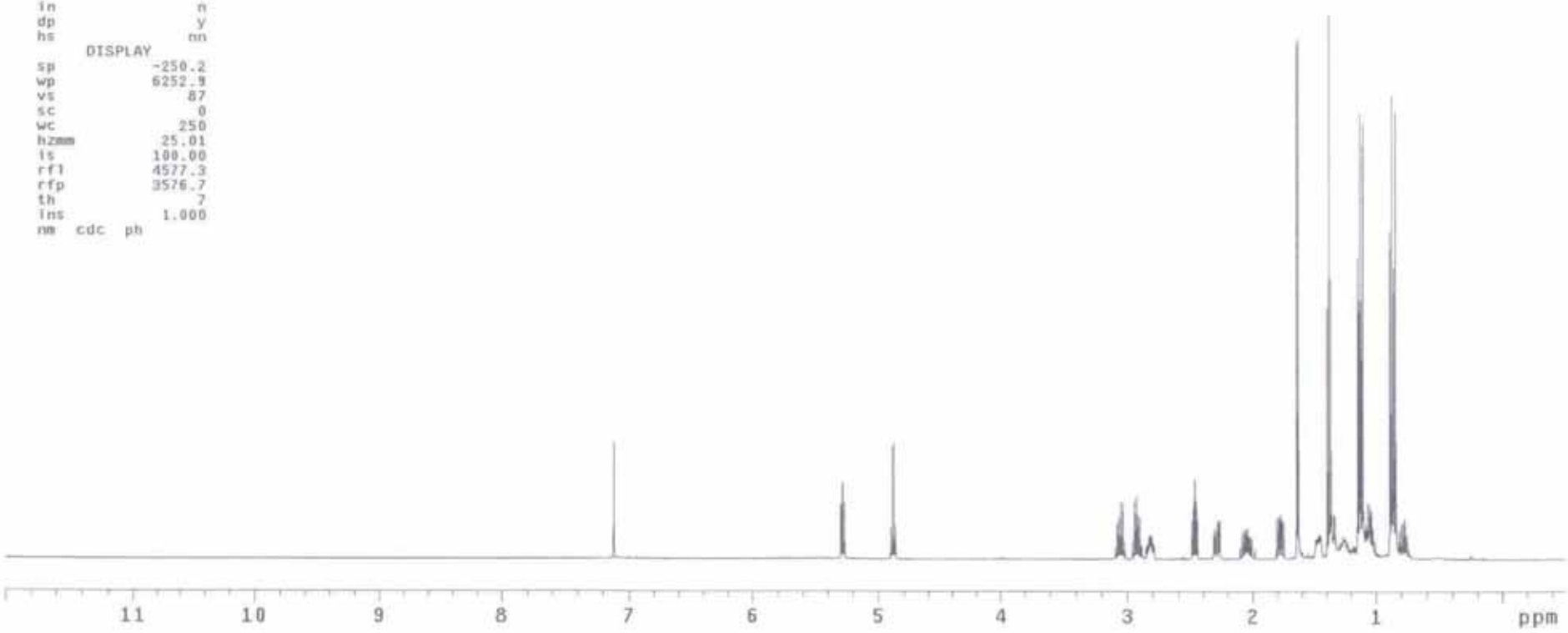
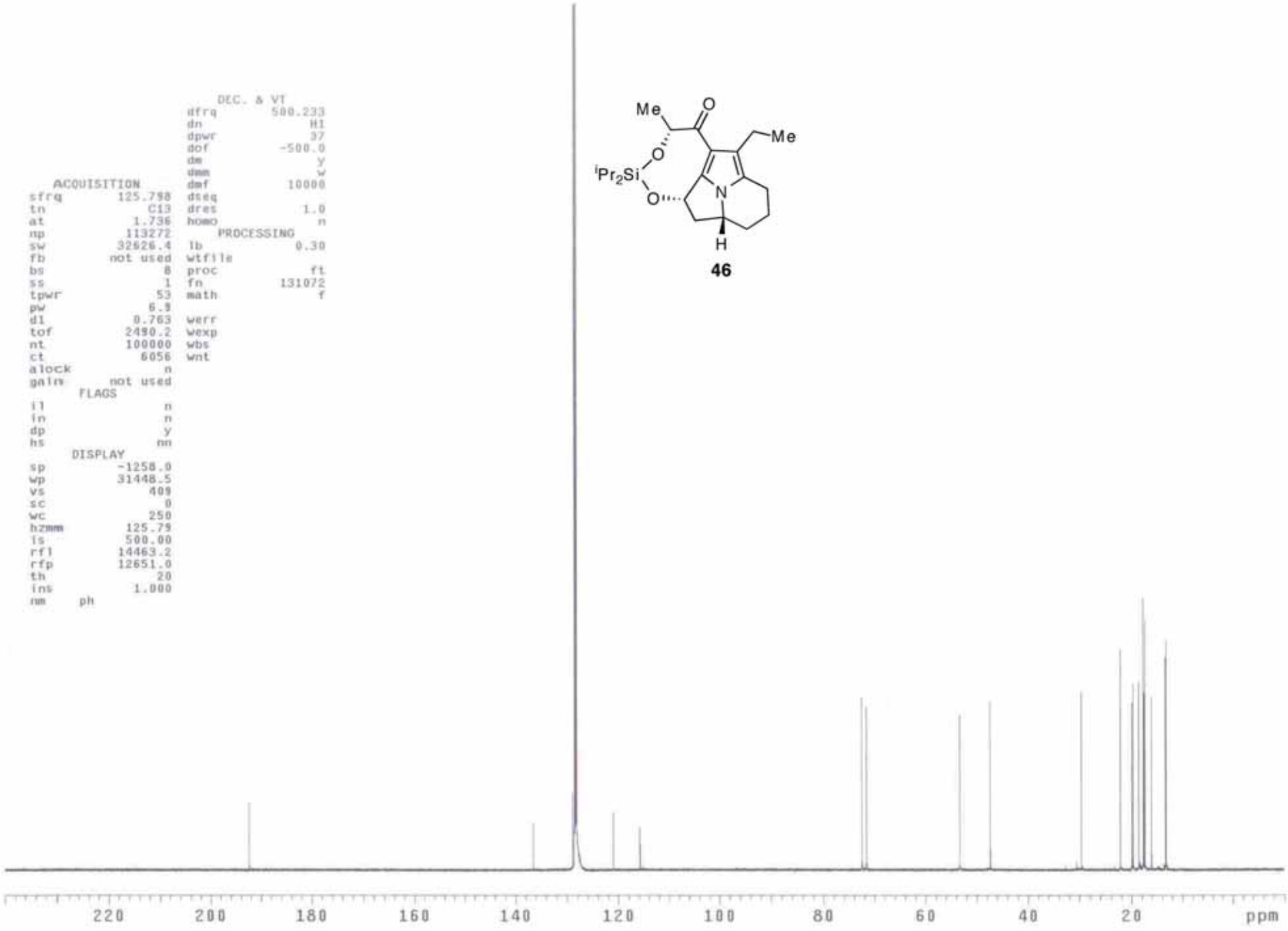



ACQUISITION
sfrq 125.798
tn C13
at 1.736
np 113272
sw 32626.4
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2490.2
nt 100000
ct 6056
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.0
wp 31448.5
vs 409
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 14463.2
rfp 12651.0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
Me
O
iPr2Si
O
N
H
46
220
200
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION	
sfrq	499.749
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	1
tpwr	56
pw	8.9
d1	1.000
tof	1519.5
nt	1000
ct	72
alock	n
gain	not used

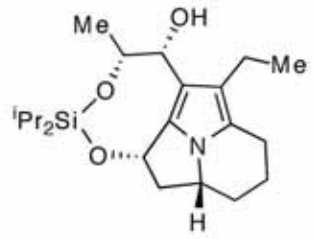
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-208.8
wp	6246.6
vs	116
sc	0
wc	250
hzmm	7.75
is	112.47
rfl	1233.8
rfp	0
th	29
ins	1.000

nm cdc ph

DEC. & VT	
dfrq	125.673
dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
lb	0.01
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	wft



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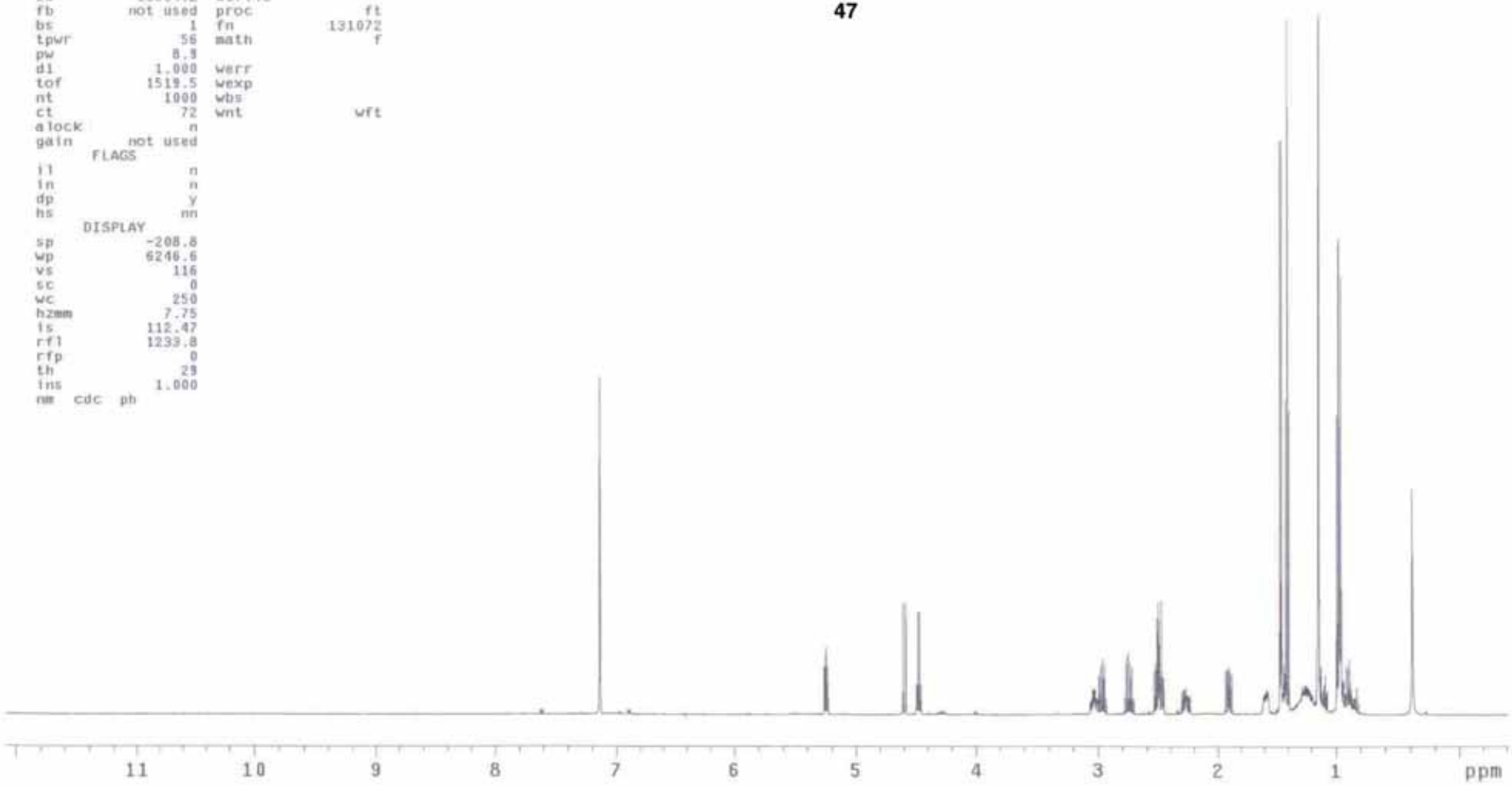
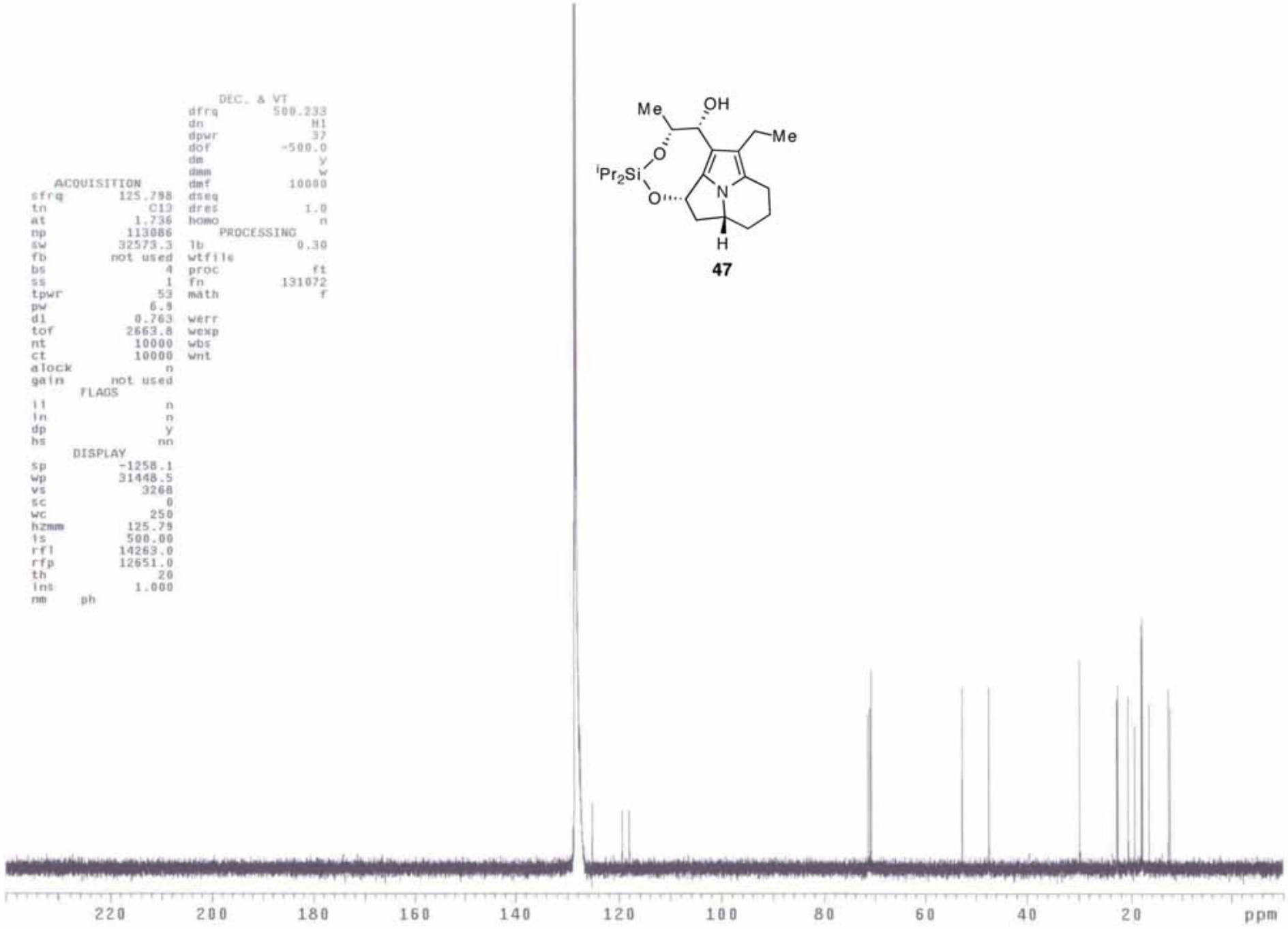
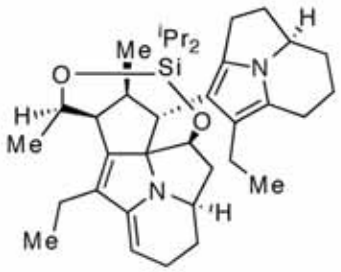



ACQUISITION
sfrq 125.798
tn C13
at 1.736
np 113086
sw 32573.3
fb not used
bs 4
ss 1
tpwr 53
pw 6.8
d1 0.763
tof 2663.8
nt 10000
ct 10000
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.1
wp 31448.5
vs 3268
sc 0
wc 250
hzmm 125.79
is 500.00
rfl 14263.0
rfp 12651.0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
OH
Me
iPr2Si
O
O
N
H
47
220
200
180
160
140
120
100
80
60
40
20
ppm



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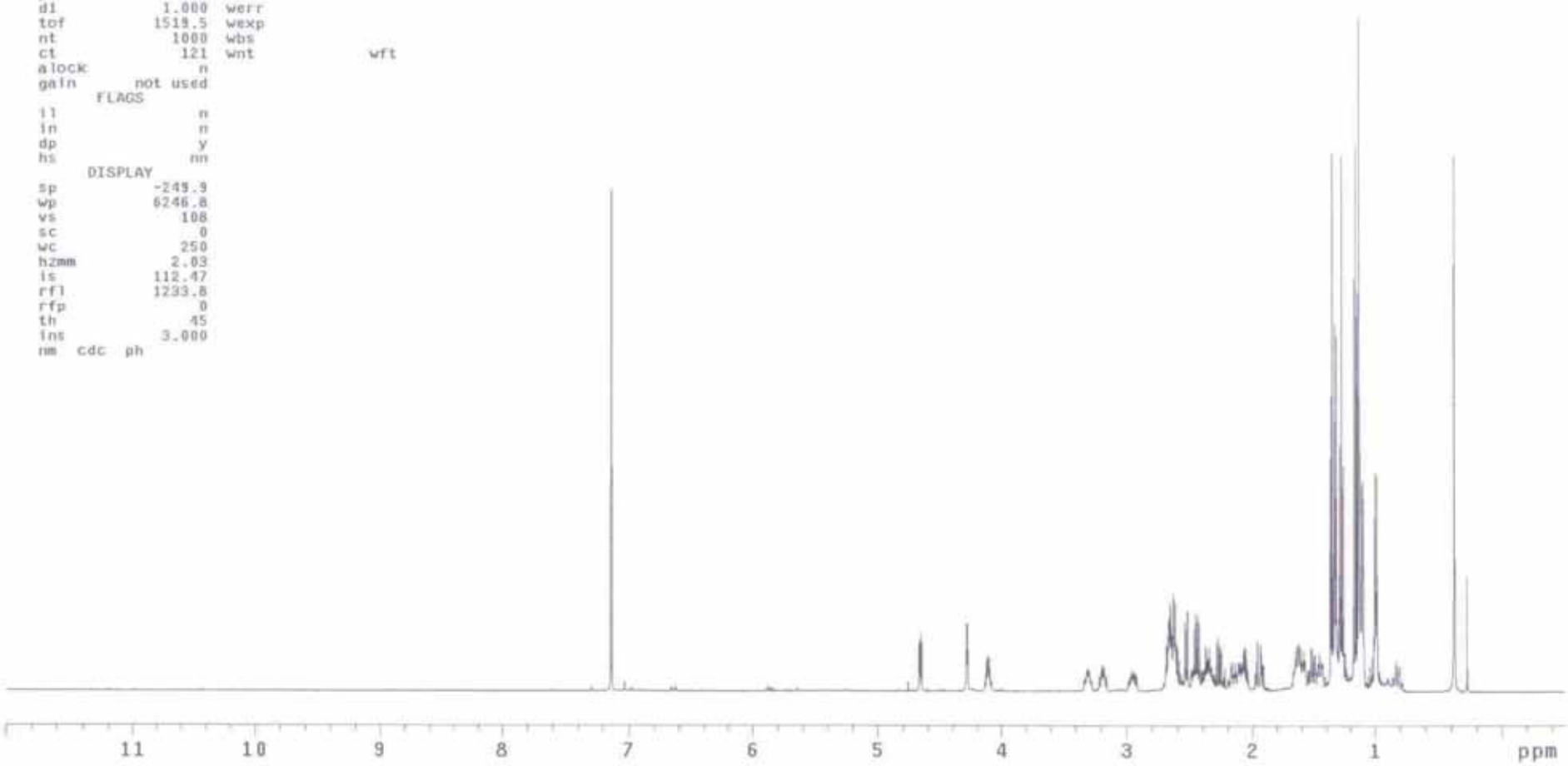
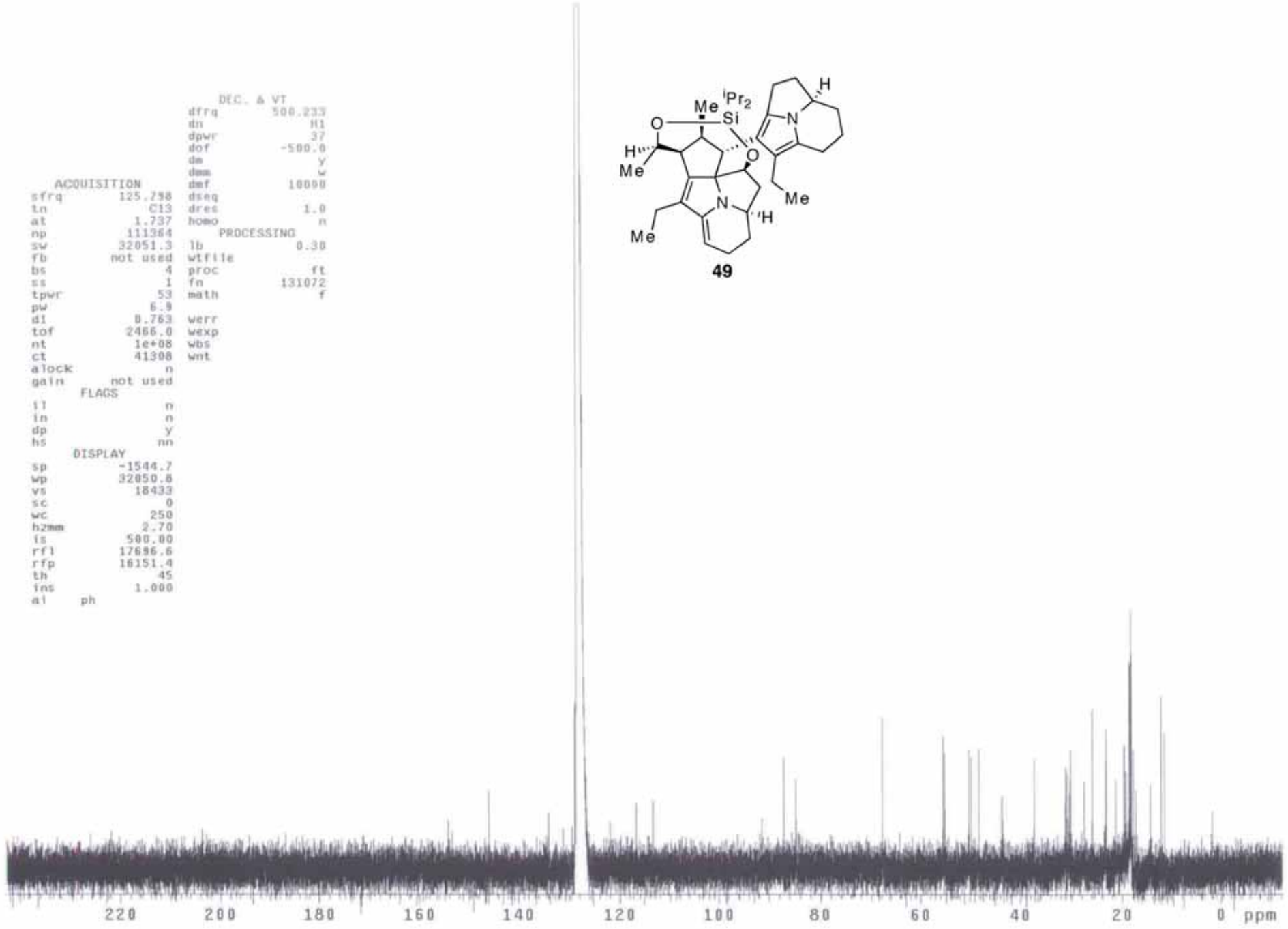
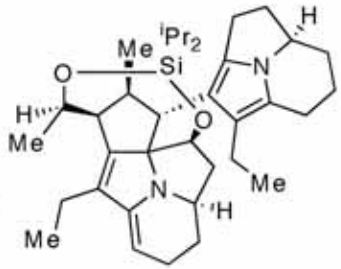
ACQUISITION		DEC. & VT	
sfrq	499.749	dfrq	125.673
tn	H1	dn	C13
at	3.001	dpwr	30
np	63050	dof	0
sw	10504.2	dm	nnn
fb	not used	dmm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.9	dres	1.0
d1	1.000	homo	n
tof	1519.5	PROCESSING	
nt	1000	wtfile	
ct	121	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	wft
hs	nn		
DISPLAY			
sp	-249.9		
wp	6246.8		
vs	108		
sc	0		
wc	250		
hzmm	2.03		
is	112.47		
rfl	1233.8		
rfp	0		
th	45		
ins	3.000		
nm cdc ph			




ACQUISITION
sfrq 125.798
tn C13
at 1.737
np 111364
sw 32051.3
fb not used
bs 4
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2466.0
nt 1e+08
ct 41308
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1544.7
wp 32050.8
vs 18433
sc 0
wc 250
hzmm 2.70
is 500.00
rfl 17696.6
rfp 16151.4
th 45
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10090
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
iPr2
Si
O
H
Me
O
N
H
N
H
Me
Me
49
220
200
180
160
140
120
100
80
60
40
20
0
ppm

PULSE SEQUENCE: gCOSY
Relax. delay 1.000 sec
Acq. time 0.248 sec
Width 4128.8 Hz
2D Width 4128.8 Hz
12 repetitions
128 increments
OBSERVE H1, 499.7446871 MHz
DATA PROCESSING
Sq. sine bell 0.124 sec
F1 DATA PROCESSING
Sq. sine bell 0.031 sec
FT size 2048 x 2048
Total time 0 min, -1 sec



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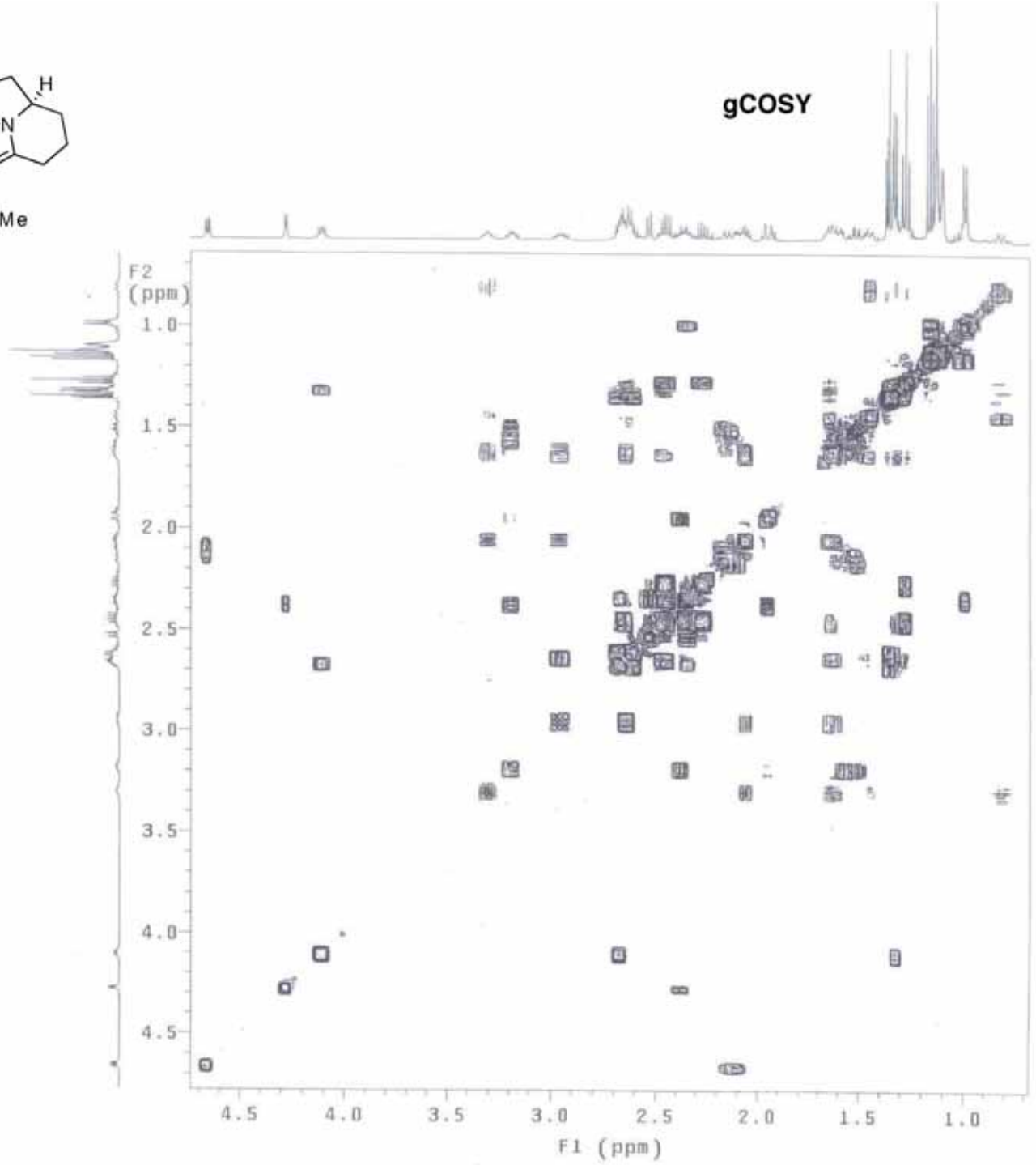
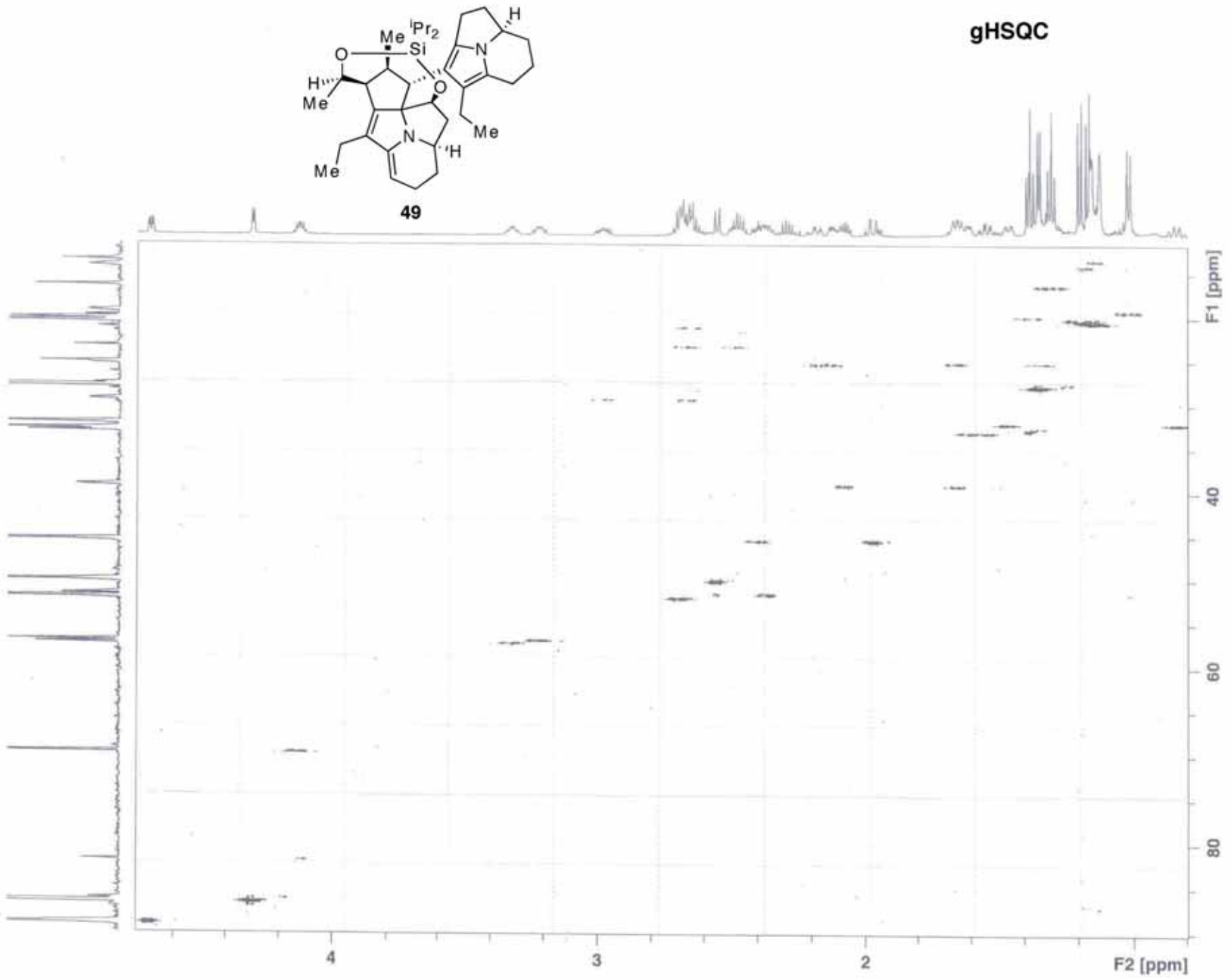
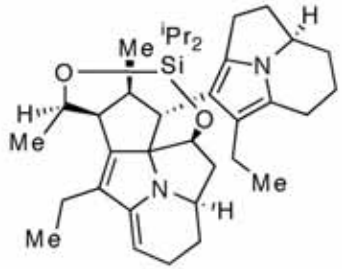
gCOSY




gHSQC
Me
iPr2
Si
O
H
Me
O
N
H
Me
N
H
Me
Me
49
F1 [ppm]
40
60
80
4
3
2
F2 [ppm]



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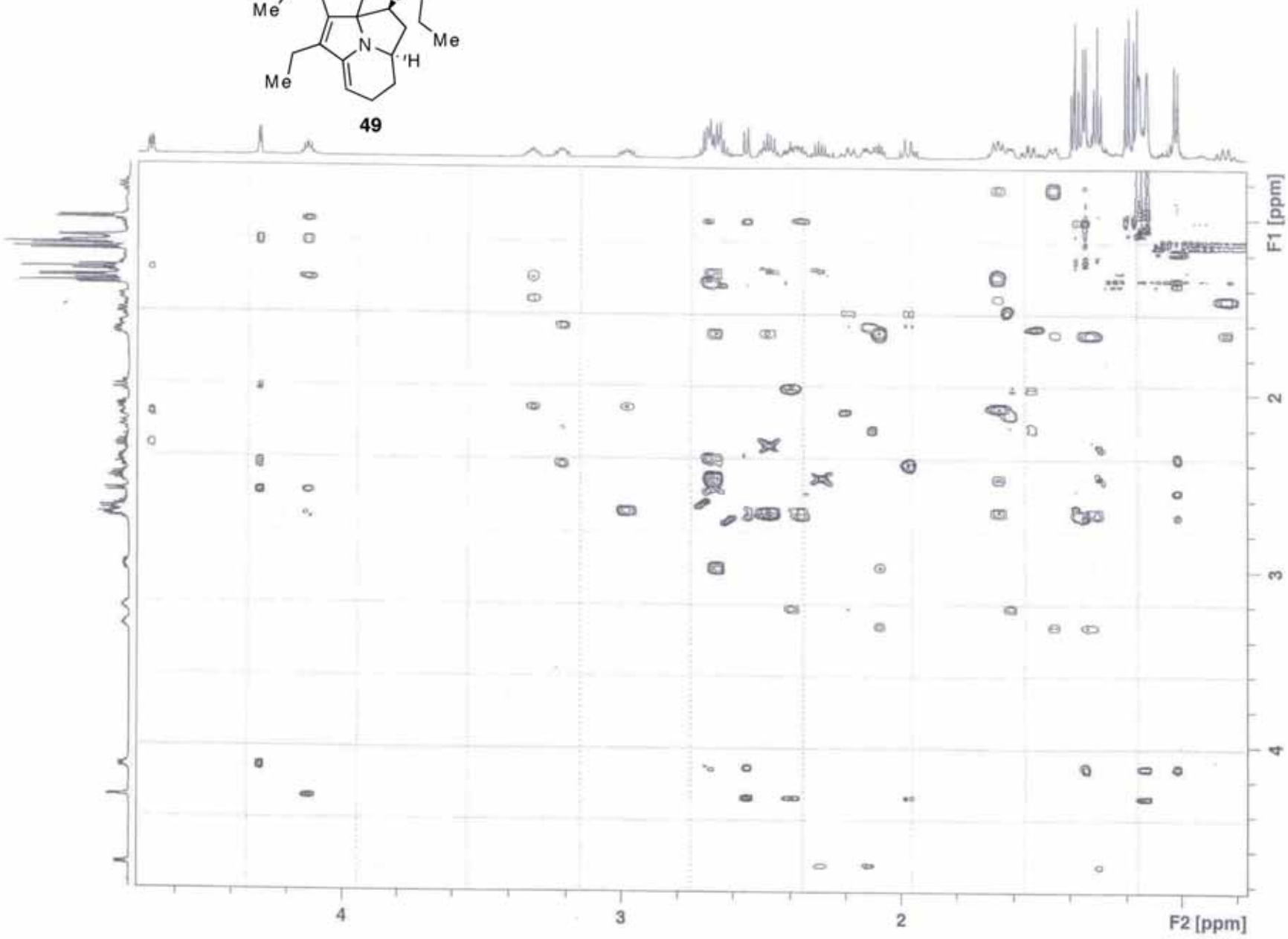
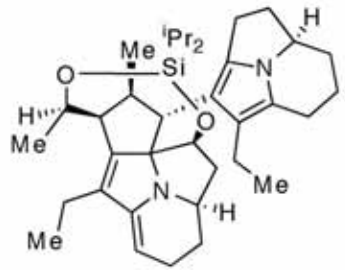
NOESY





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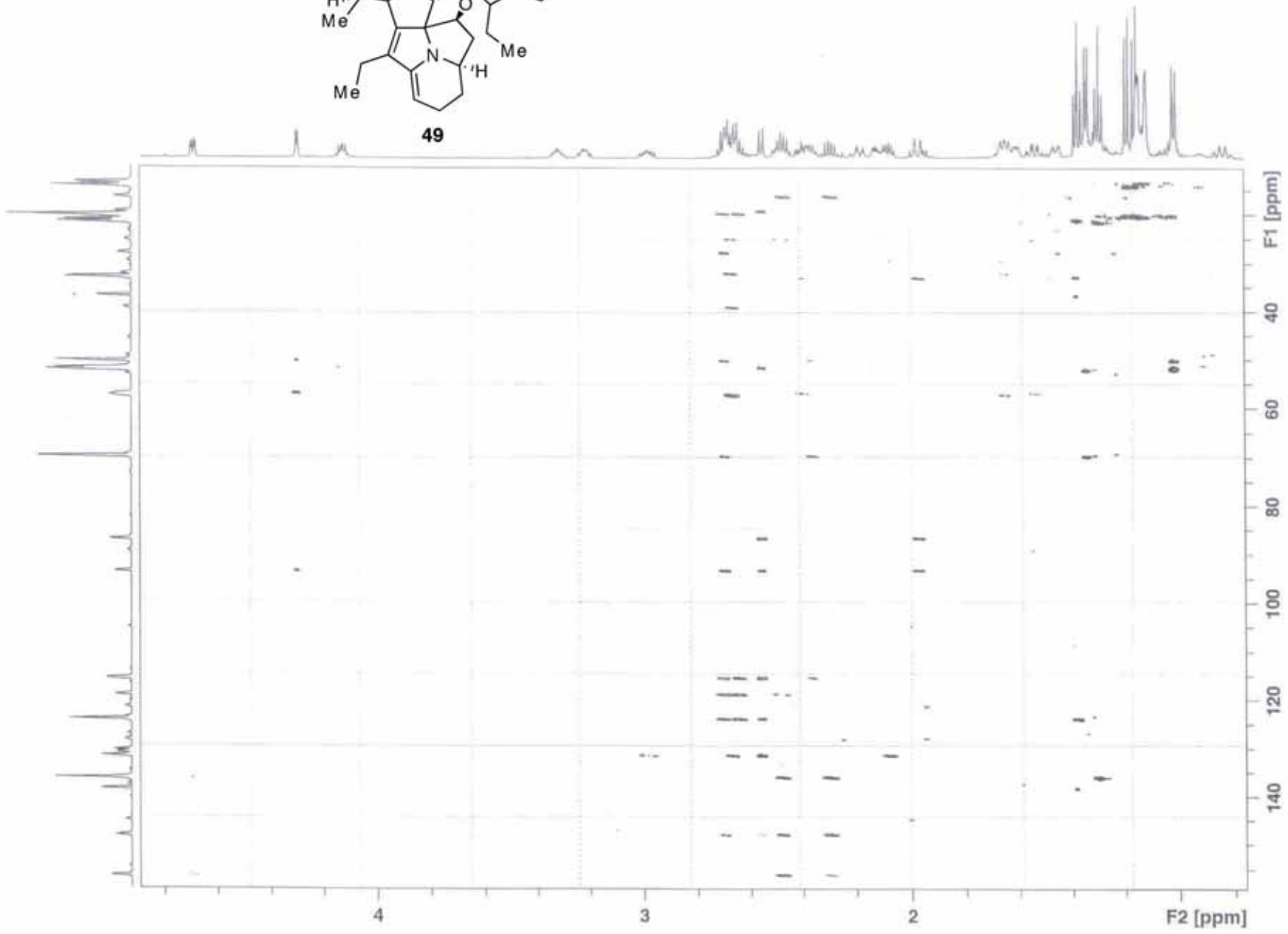
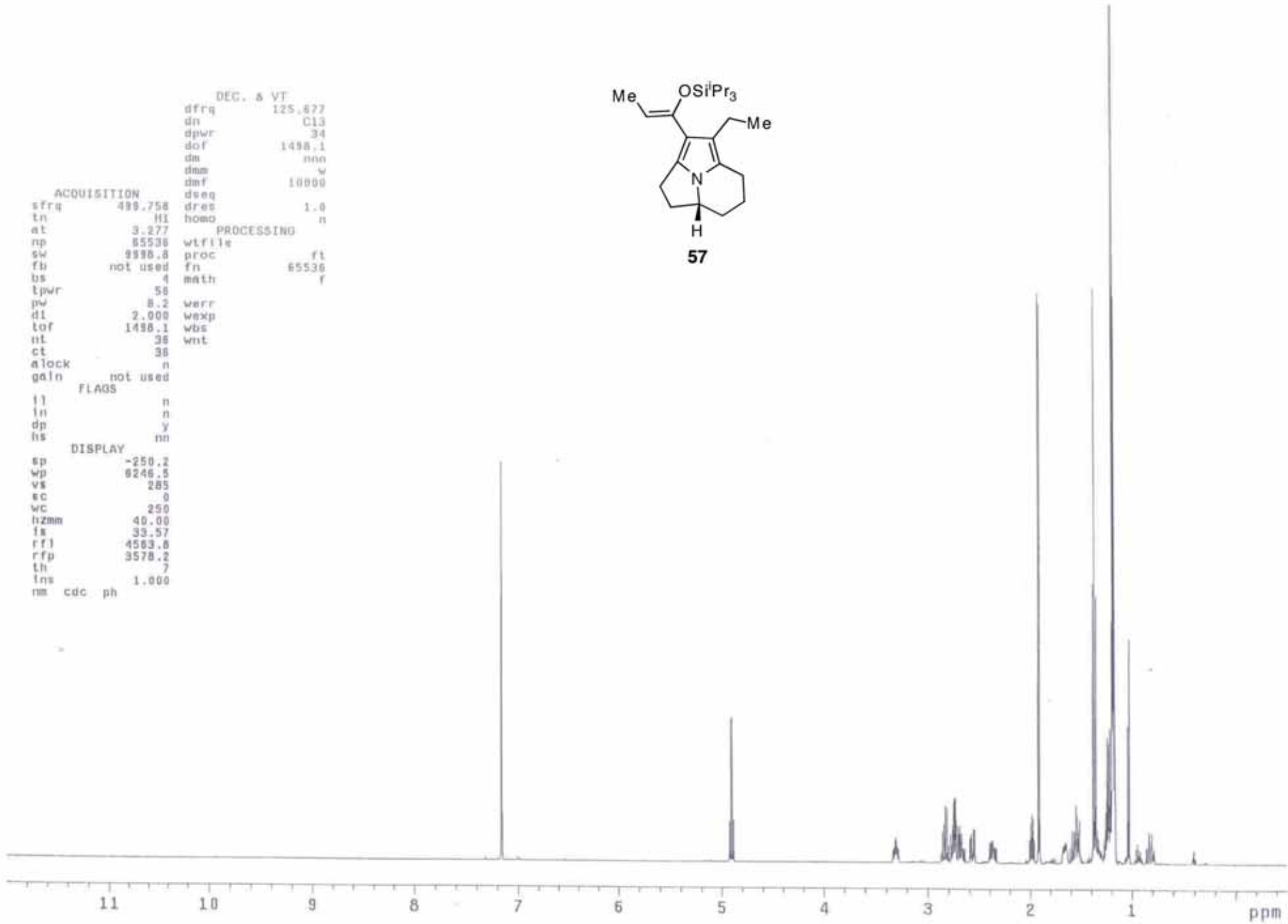
gHMBC




ACQUISITION
sfrq 499.758
tn H1
at 3.277
np 65536
sw 9998.8
fb not used
bs 4
tpwr 58
pw 8.2
d1 2.000
tof 1498.1
nt 36
ct 36
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6246.5
vs 285
sc 0
wc 250
hzmm 40.00
is 33.57
rfl 4563.8
rfp 3578.2
th 7
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.677
dn C13
dpwr 34
dof 1498.1
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 65536
math f
werr
wexp
wbs
wnt
Me
OSi^{i}Pr$_3$
Me
N
H
57
11
10
9
8
7
6
5
4
3
2
1
ppm

ACQUISITION	
sfrq	125.798
tn	C13
at	1.738
np	131010
sw	37735.8
fb	not used
bs	8
ss	1
tpwr	53
pw	6.9
d1	0.783
tof	631.4
nt	10000
ct	2832
alock	n
gain	not used

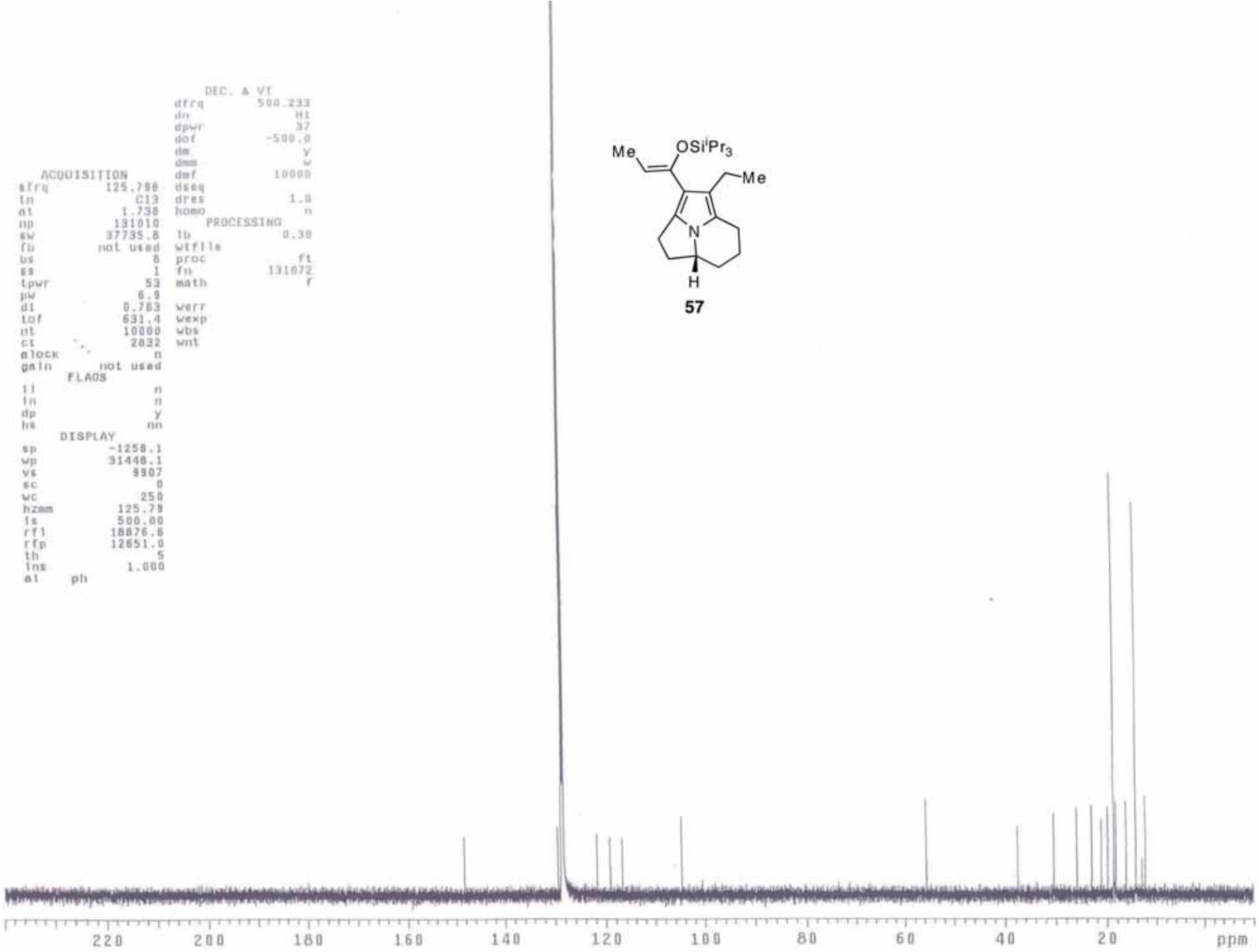
FLAGS	
il	n
in	n
dp	y
hs	nn

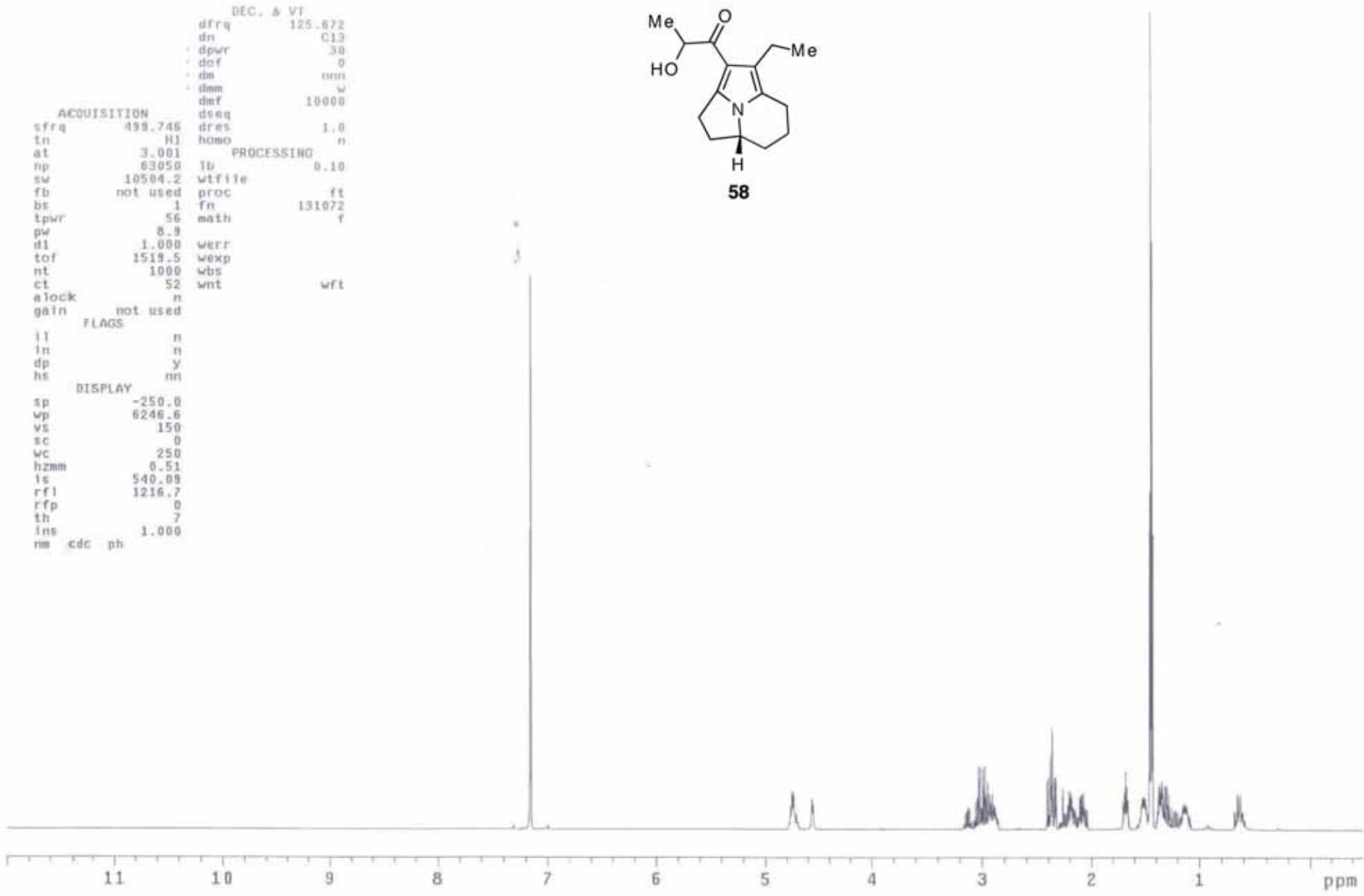
DISPLAY	
sp	-1258.1
wp	31448.1
vs	9907
sc	0
wc	250
hzmm	125.79
is	500.00
rf1	18876.6
rfp	12651.0
th	5
lns	1.000
al	ph

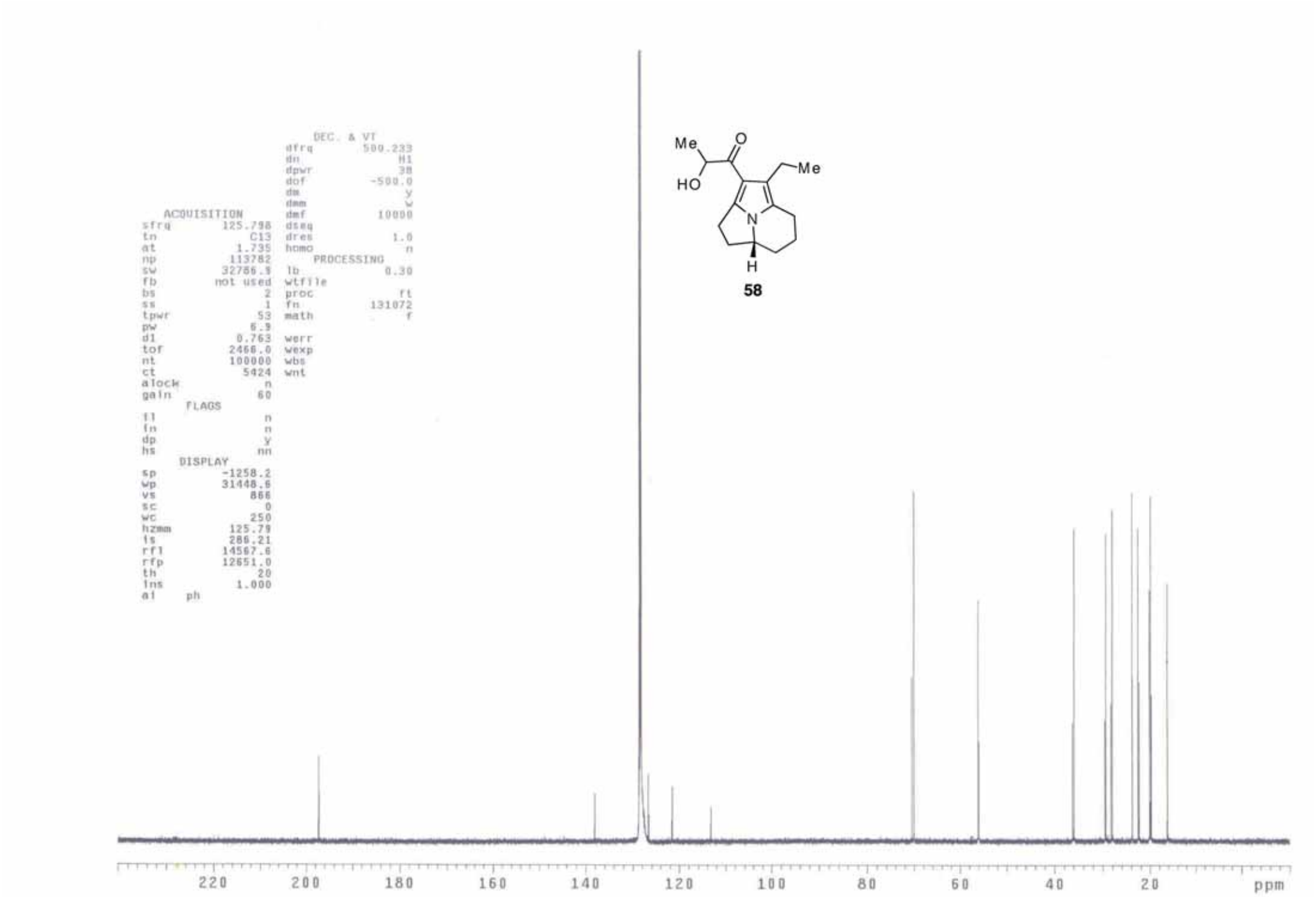
DEC. & VT	
dfrq	500.233
dn	H1
dpwr	37
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
lb	0.30
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	

57




DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.10
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft
ACQUISITION
sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.9
d1 1.000
tof 1519.5
nt 1000
ct 52
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.6
vs 150
sc 0
wc 250
hzmm 0.51
is 540.09
rfl 1216.7
rfp 0
th 7
ins 1.000
nm cdc ph
Me
O
HO
Me
N
H
58
11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.798
tn C13
at 1.735
np 113782
sw 32786.9
fb not used
bs 2
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 2466.0
nt 100000
ct 5424
alock n
gain 60
FLAGS
fl n
fn n
dp y
hs nn
DISPLAY
sp -1258.2
wp 31448.6
vs 866
sc 0
wc 250
hzmm 125.79
is 286.21
rfl 14567.6
rfp 12651.0
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 38
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
HO
Me
N
H
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180
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80
60
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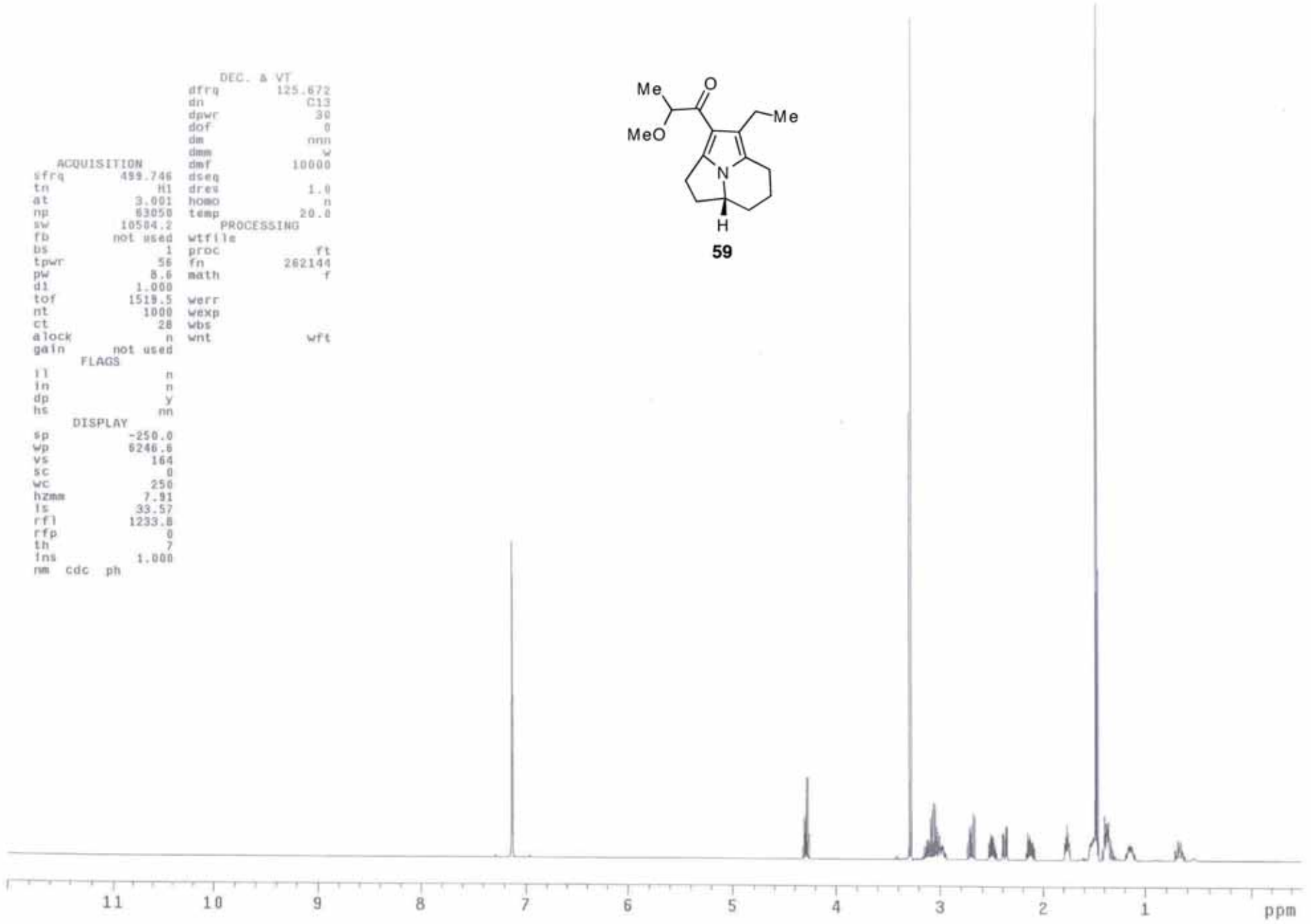
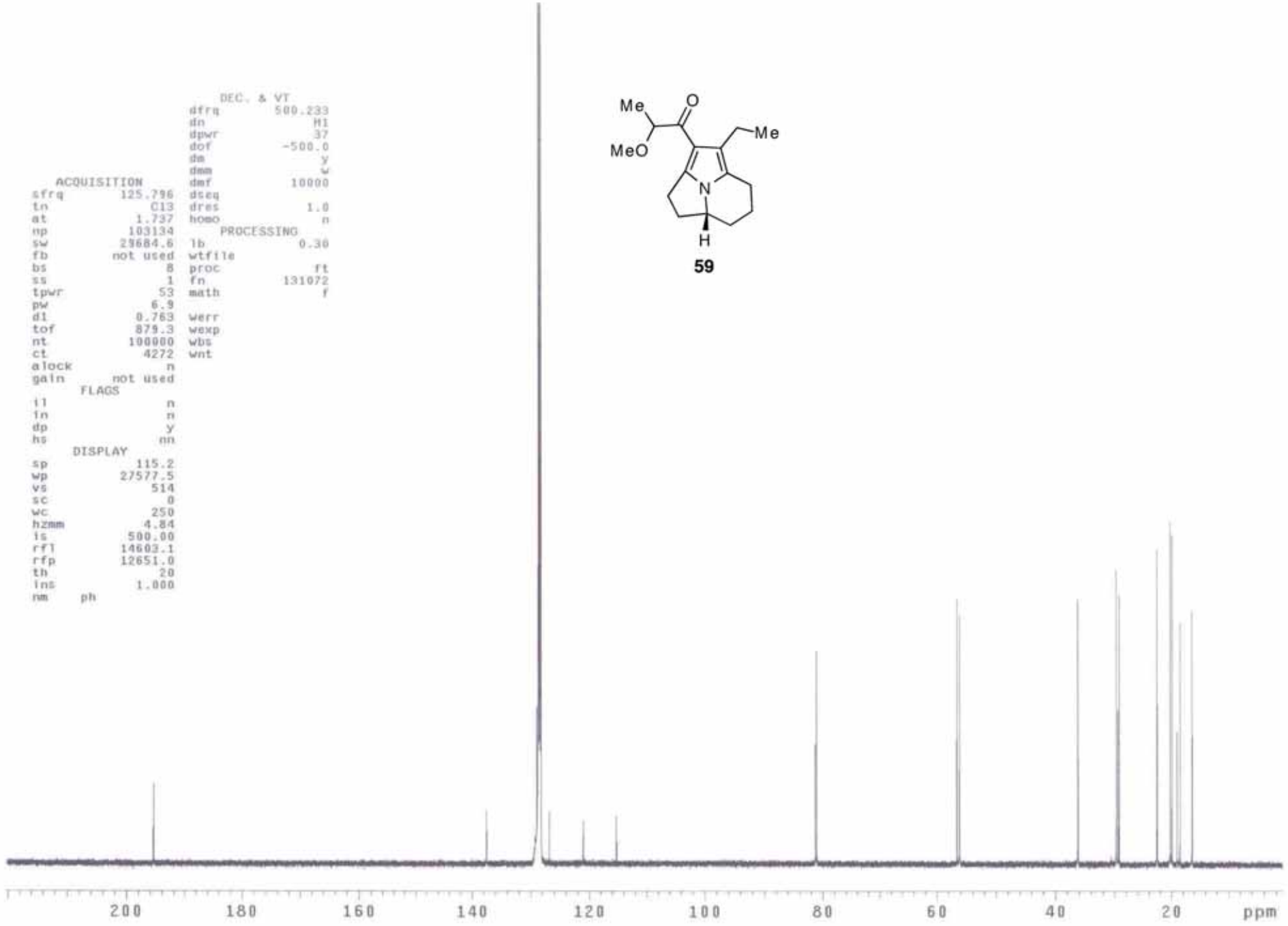
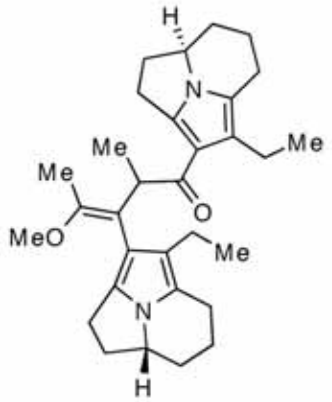
20
ppm


ACQUISITION
sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.6
d1 1.000
tof 1519.5
nt 1000
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.6
vs 164
sc 0
wc 250
hzmm 7.91
is 33.57
rfl 1233.8
rfp 0
th 7
ins 1.000
nm cdc ph
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 20.0
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
Me
O
MeO
Me
N
H
59
11
10
9
8
7
6
5
4
3
2
1
ppm


ACQUISITION
sfrq 125.796
tn C13
at 1.737
np 103134
sw 29684.6
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 879.3
nt 100000
ct 4272
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 115.2
wp 27577.5
vs 514
sc 0
wc 250
hzmm 4.84
is 500.00
rfl 14603.1
rfp 12651.0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
O
MeO
Me
N
H
59
200
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION		DEC. & VT	
sfrq	499.745	dfrq	125.674
tn	H1	dn	C13
at	3.000	dpwr	38
np	41840	dof	1519.5
sw	6873.5	dm	nnn
fb	not used	dmm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.3	dres	1.0
d1	1.000	homo	n
tof	291.0	PROCESSING	
nt	100000	lb	0.01
ct	65	wtfile	
alock	n	proc	ft
gain	not used	fn	131072
FLAGS		math	f
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	wft
DISPLAY			
sp	-250.8		
wp	6246.7		
vs	106		
sc	0		
wc	250		
hzmm	1.04		
is	53.01		
rfl	680.1		
rfp	0		
th	7		
ins	1.000		
nm cdc ph			



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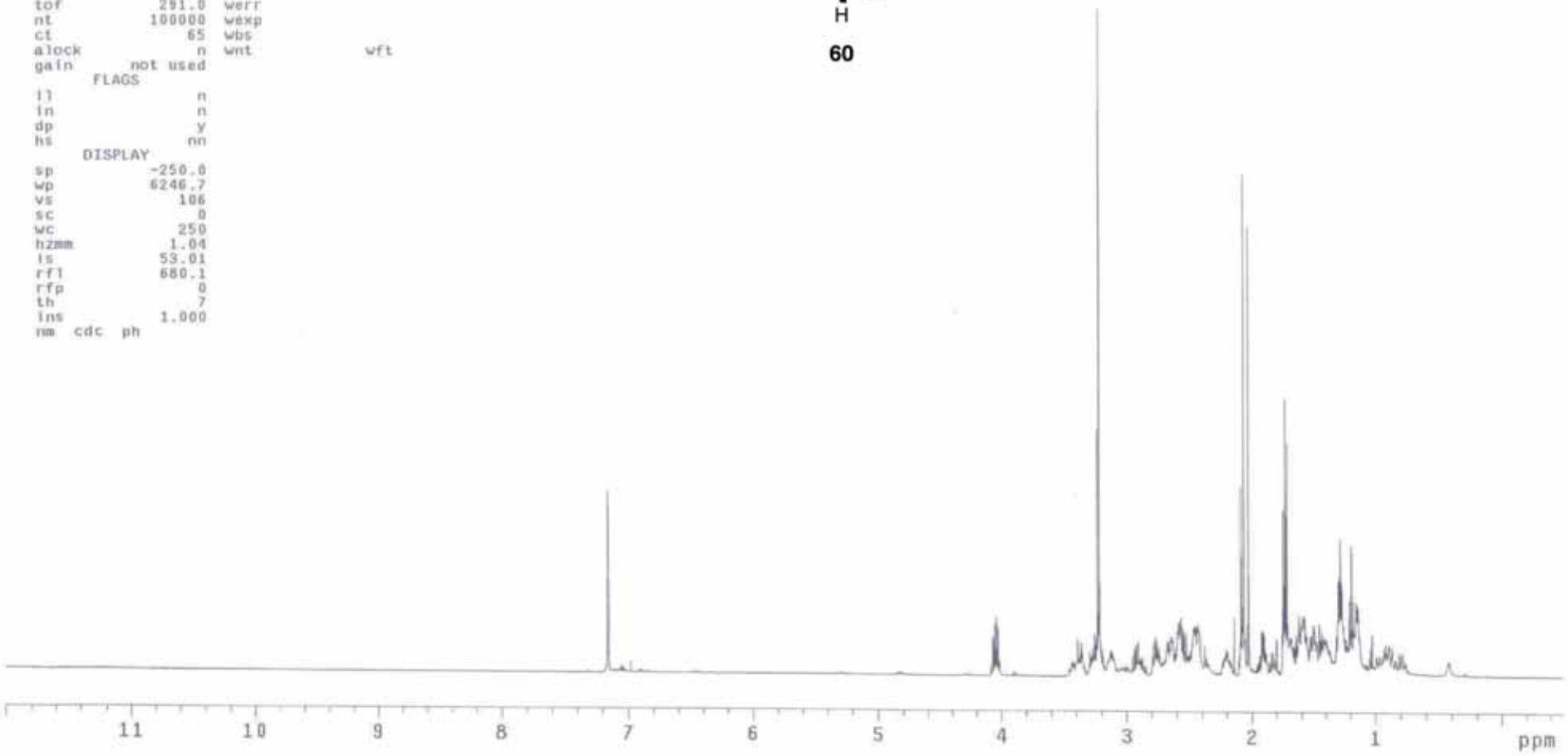
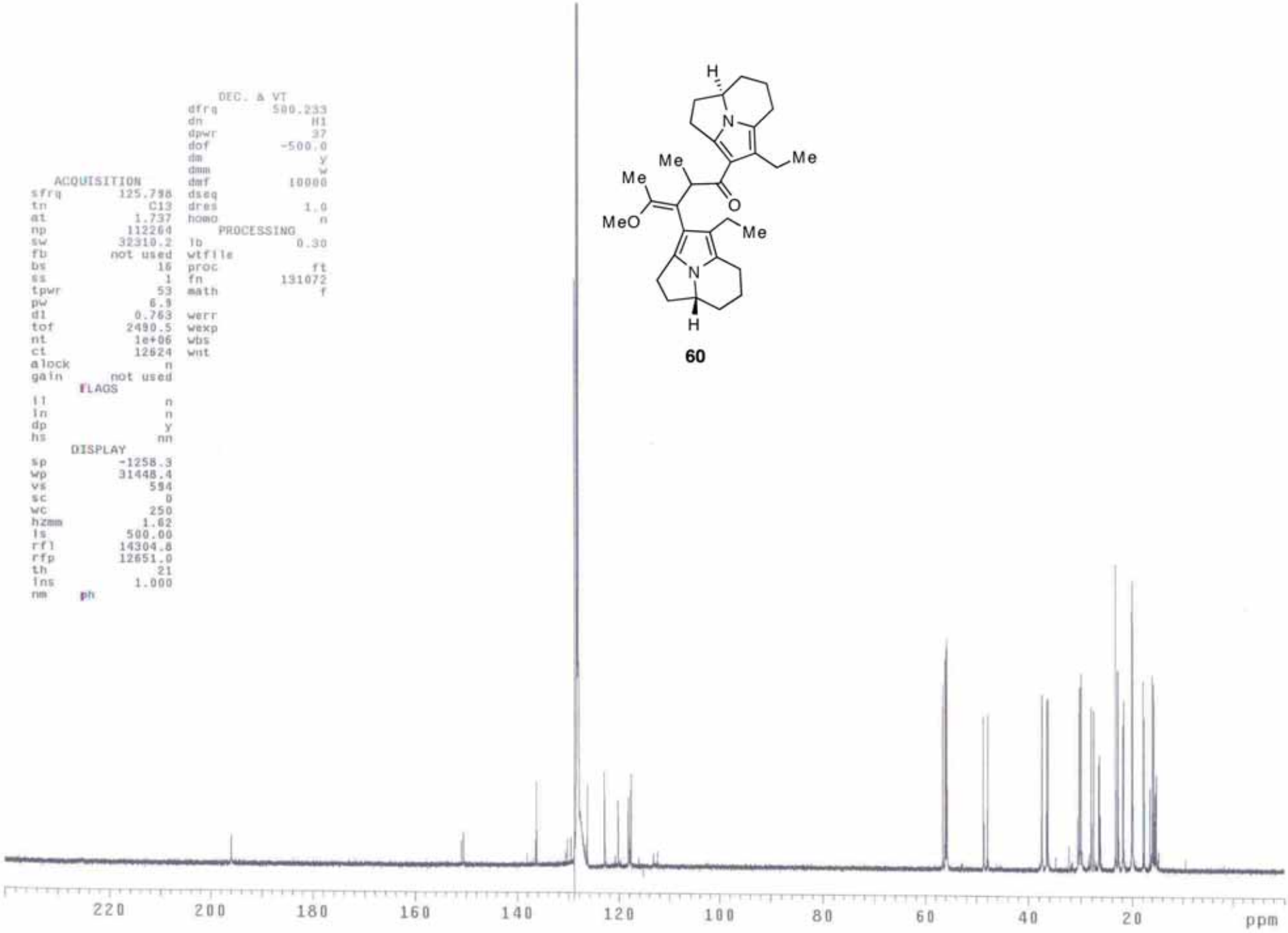



ACQUISITION
sfrq 125.798
tn C13
at 1.737
np 112264
sw 32310.2
fb not used
bs 16
ss 1
tpwr 53
pw 6.9
dl 0.763
tof 2490.5
nt 1e+06
ct 12624
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1258.3
wp 31448.4
vs 594
sc 0
wc 250
hzmm 1.62
is 500.00
rfl 14304.8
rfp 12651.0
th 21
ins 1.000
nm ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
H
N
Me
Me
Me
O
MeO
Me
N
H
60
220
200
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION	
sfrq	500.235
tn	H1
at	3.200
np	64000
sw	10000.0
fb	not used
bs	1
ss	1
tpwr	55
pw	9.0
dl	0
tof	1498.2
nt	16
ct	14
alock	n
gain	not used

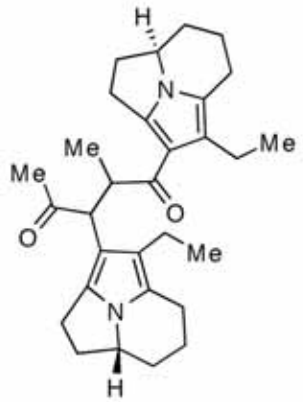
FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-250.2
wp	6252.7
vs	94
sc	0
wc	250
hzmm	9.33
is	100.00
rfl	4577.3
rfp	3576.7
th	7
ins	1.000

nm cdc ph

DEC. & VT	
ifrq	125.755
in	C13
ipwr	37
iof	0
lm	nnn
lmm	c
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



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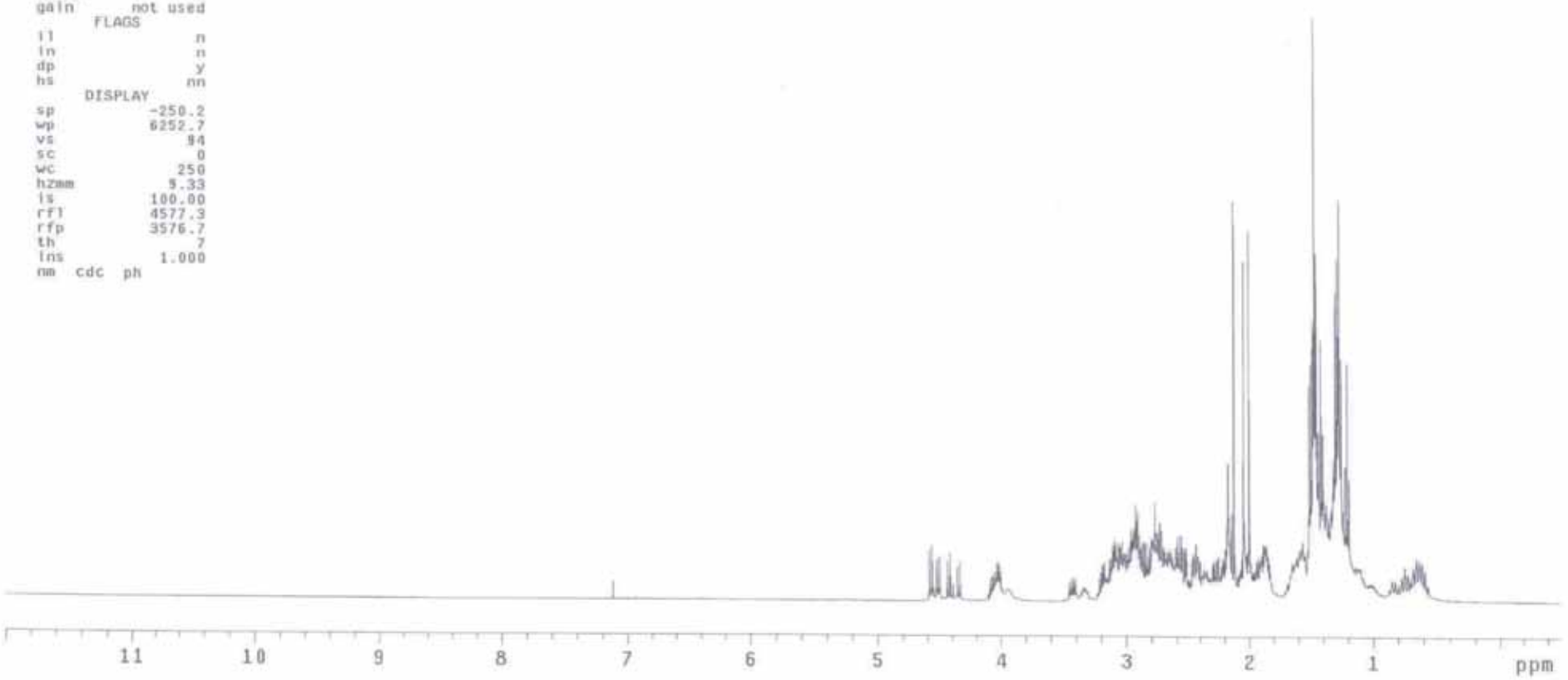

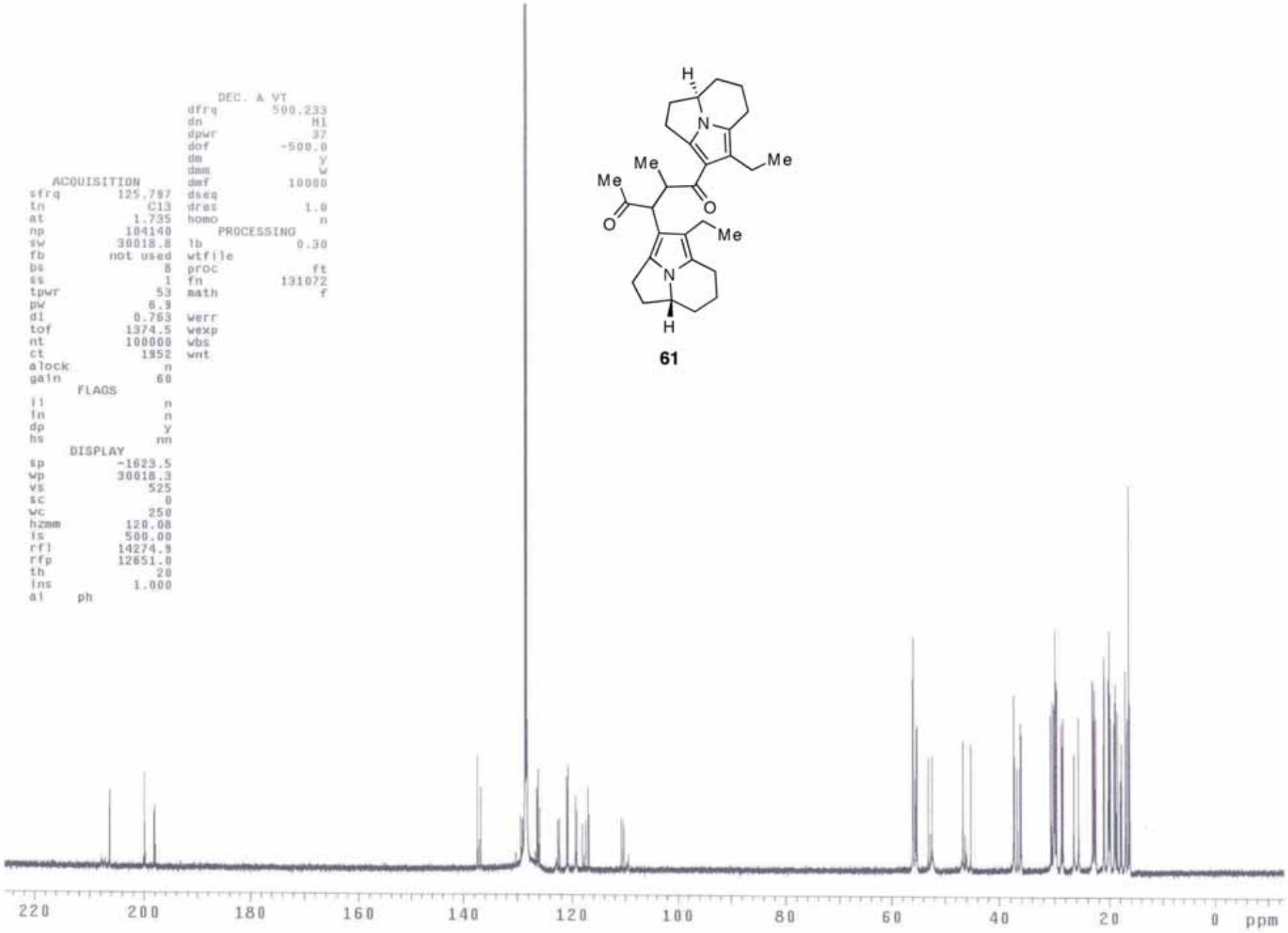
ACQUISITION
sfrq 125.797
tn C13
at 1.735
np 104140
sw 30018.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 1374.5
nt 100000
ct 1952
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1623.5
wp 30018.3
vs 525
sc 0
wc 250
hzmm 120.08
is 500.00
rfl 14274.9
rfp 12651.0
th 20
ins 1.000
ai ph
DEC. A VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
H
N
Me
Me
Me
O
O
Me
N
H
61
220
200
180
160
140
120
100
80
60
40
20
0
ppm